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September 24 - 27, 1996

Albuquerque, NM

Volume II

Edited by
Kerry L. Sublette

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The University of Tulsa Division of Continuing Education
and College of Engineering and Applied Sciences and
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Chair: Kerry L. Sublette
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Treatment and Disposal of Sulfur Compounds

Sulfide Bioscavenging Of Sour Produced Water By Natural Microbial Populations

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ABSTRACT

Oxidation of sulfide in produced brine collected from the Coleville field in Saskatchewan, Canada was studied in enrichment cultures and corefloods. Addition of 5 mM KNO_3 and 100 micromolar NaH_2PO_4 to brine enrichments resulted in bio-oxidation of 3.3 mM sulfide. Reaction products were identified as elemental sulfur, nitrite and nitrogen gas. Sulfide oxidation was complete as rapidly as 7 hours, following a variable lag time. The stoichiometry of the reaction indicated that 1.6 mmoles of sulfide were oxidized per mmole of nitrate added. Sulfide oxidation rates of 1 to 5 mmol L^{-1} h^{-1} were observed in corefloods inoculated with Coleville brine. Effluent concentrations of nitrite suggested that reduction of the nitrite was rate limiting. No significant loss of core permeability resulted from the production of bacteria and elemental sulfur. These results suggest that bio-oxidation of soured produced water by naturally occurring microbial populations can be used for in-situ remediation of soluble sulfide in the Coleville reservoir.

INTRODUCTION

Sour produced water results from the production of hydrogen sulfide (H_2S) in the reservoir, wellbore or surface facilities. The source of H_2S is frequently the result of the metabolic activity of sulfate-reducing bacteria (SRB) or other sulfidogenic bacteria. The presence of sulfides ($S^=$, HS^-, H_2S) in produced fluids causes operational problems resulting in corrosion, unsafe working conditions and formation plugging due to build-up of iron sulfide scale.

Sulfide scavengers are sometimes used to remediate the effects of sulfides in reservoirs. Sulfide scavengers used to treat reservoirs remove sulfides by either forming adducts, precipitates or oxidation products of sulfides (e.g., elemental sulfur) (1). Problems associated with the use of these chemical scavengers include: interference by other compounds (i.e., non-selective), partitioning into the oil phase, incompatibility with brines, generation of by-products requiring disposal, reversibility, corrosive activity, costly, hazardous and harmful effects to the environment. In addition, scavengers are designed to treat the symptoms of biosouring, and not the cause.

Sulfide bioscavengers (SBSs) comprise microorganisms that remediate sulfide through the bio-oxidation of sulfides to more oxidized sulfur species. The bio-oxidant can be either in the form of oxygen or some water-soluble oxyanion, such as nitrate. Bioscavengers have the advantages of being selective for sulfides, low in toxicity, non-hazardous, environmentally friendly and inexpensive.

Nitrate-reducing bacteria (NRB) that oxidize sulfide while reducing nitrate to ammonia or nitrogen gas are particularly attractive for use as SBSs. NRB offer the additional advantage of out-competing SRB for their food source once the sulfide has been remediated thereby controlling further production of sulfide (2,3). Either indigenous NRB or non-indigenous NRB can be used. Sublette et al.(4) amended a sour produced water stream with non-indigenous NRB, *Thiobacillus denitrificans* strain F, to effectively remediate sulfide, while McInerney et al.(5) injected ammonium nitrate into the producing reservoir of the Southeast Vasser Vertz Sand Unit in Payne County, Oklahoma and reported a 40 to 60% reduction in soluble sulfide at three adjacent producers attributed to indigenous NRB. More recently, Gevertz et al.(6) reported that batch-treatment of three producing wells at the Coleville Unit in Saskatchewan, Canada with nitrate and phosphate stimulated indigenous NRB populations, resulting in a 90% reduction in soluble sulfide in two of the wells, and sustained sulfide reductions of 50% for several days following start-up of the producers. Importantly, no increase in SRB populations was observed. This suggested that the remaining 50% of the sulfide was being transported through the reservoir and may not be controlled through local batch treatment. Therefore the effective scavenging of sulfide would require treatment of injected water, as well.

The objective of this study was to determine the stoichiometry of the bio-oxidation reaction in Coleville enrichments and assess the kinetics, and efficiency of sulfide oxidation as well as its impact on injectivity and permeability of a

porous medium. This information is needed to design a field test for in-situ treatment of injected water.

MATERIALS AND METHODS

Enrichments

Brine was collected from the free-water-knockout (FWKO) at the Coleville Unit in deoxygenated, sterile, screw-capped, glass-bottles containing a butyl rubber septum. Bottles were shipped the day of collection and received, usually, within one week. Filtered brine was sterile-filtered through 0.2 μm membrane filters.

Enrichments using Coleville brine were prepared in sterile, 50cc serum bottles that were pre-incubated overnight in a Coy anaerobic glove box containing a gaseous atmosphere of H_2:CO_2:N_2 (10:5:85). Potassium nitrate, potassium nitrite, and sodium phosphate (monobasic) were added to bottles from sterile stock solutions. Bottles were stoppered with butyl rubber stoppers, crimp sealed and incubated at 30°C.

Sulfide was determined colorimetrically by a modification of the method of Fogo and Popowski(7), where sulfide was trapped by reaction with zinc acetate (final concentration 0.02%). Nitrate, nitrite, sulfate, and sulfite were separated by ion chromatography and detected amperometrically. Ammonium was determined using an ammonia ion specific electrode and total soluble sulfur (TSS) by x-ray fluorescence (nearest 5 ppm). The presence of elemental sulfur and calcite was visualized by scanning electron microscopy and confirmed via electron dispersion spectroscopy.

Bottle counts of NRB and SRB were determined by performing tenfold serial dilutions of samples in serum bottles containing the appropriate culture media. SRB were cultured in API RP38 media (C&S Laboratories, Tulsa, OK) and NRB in sterile-filtered FWKO brine amended with 5 mM KNO_3, 100 μM NaH_2PO_4 and 0.001% resazurin. A positive NRB bottle would turn from colorless to pink. Each positive bottle represents and approximate tenfold increase in cell number.

Determination of ^{15}N-labeled headspace gases was performed with Coleville enrichments set up containing: a) 100 μM NaH_2PO_4; b) same as a) with 5 mM $K^{15}NO_3$; and c) same as b) except the brine was filtered (0.2 μm membrane filters) to remove the indigenous bacteria. The presence of $^{15}N_20$, ^{15}NO, and $^{15}N_2$ was determined by gas chromatography/mass spectroscopy.

Coreflood

A 1288 mD ceramic core (P-40-C, Coors Ceramics, Golden, CO), 2.54 x 19.1 cm was fitted with end plates and epoxy-coated. Nylon tubing and fittings (1/8" ID) were attached to inlet and outlet ends of core. Pressure taps were positioned along its length at 3.8, 8.9 and 14 cm from the inlet. The core was vacuum saturated with Coleville synthetic brine (CSB) (all g/L; $MgSO_4 \cdot 7H_2O$, 0.68; $CaCl_2$, 0.14; NH_4Cl, 0.02; NaCl, 7.0) and the pore volume (PV) determined as the wet weight - dry weight / brine density (PV ≈ 44 cc). The core was then placed in a stainless steel accumulator filled with water and pressurized up to 1000 psig. Inlet tubing, outlet tubing and tubing to side pressure taps were all run out of the accumulator via a pass-through fitting at the top of the accumulator. The core was warmed to 30°C and a pore pressure of 500 psig was established in the core using a back-pressure regulator at the outlet end and flowing CSB through the core at 1 ml/min with a positive displacement pump. CSB was pumped into the core from a reservoir contained in the Coy glove box. Differential pressures along the core was measured with pressure transducers (Validyne) and signals logged by a PC. Pressures were the average of six consecutive readings take at 5 minute intervals. pH measurements at the outlet were made with a pressure tolerant pH probe coupled to a Solomat 100 Datalogger. A schematic of the core apparatus is depicted in Figure 1.

Hydraulic retention time (HRT) of the core was determined by injecting a salt solution through the core at a known rate and measuring the breakthrough time by an increase in conductivity at the outlet. Sulfide, nitrite and nitrate were determined using a Aquaquant hydrogen sulfide kit (EM Sciences), Chemets nitrite kit (Chemetrics) and Szechrome NIT (Polysciences, Inc.) reagent, respectively. NRB and SRB were determined as described above.

RESULTS AND DISCUSSION

Brine Enrichments

The requirements for biological oxidation of sulfide present in CVU brine included nitrate, phosphate and indigenous bacteria (i.e., unfiltered brine). Removal of indigenous bacteria by filtration (Figure 2) or unfiltered CVU brine without nitrate did not result in sulfide oxidation (6). Nitrite, which is a known chemical sulfide scavenger, was produced as an intermediate of the biological reduction of nitrate, but had no effect on scavenging of sulfide in the presence or absence of indigenous bacteria (Fig. 2). The chemical oxidation of sulfide by nitrite may be very slow due to the relatively low reservoir temperature found in the Coleville reservoir (≈30°C).

Upon addition of 5 mM nitrate and 100 μM phosphate to Coleville brine, complete oxidation of 3 to 4 mM sulfide occurred within 24-48 hours. The difference in oxidation rates observed for two samples, taken on different days from the FWKO, was due to an extended lag time prior to oxidation (Fig. 2).

Possible reasons for this difference in lag time include: differences in the numbers of indigenous NRB; some nutritional factor that is limiting; or some inhibitory compound varies in concentration between samples. Maximum sulfide scavenging rates measured for either sample were in the range of 0.4 and 0.6 mmol sulfide/ L/h.

Reaction Stoichiometry

The fate of nitrate and sulfide in Coleville enrichments was determined by varying the amount of nitrate from 0.7 to 5.6 mM (Table 1). Complete oxidation of sulfide occurred at all nitrate concentrations tested except 0.7 mM, where 1.7mM sulfide was still detected after 72 hours incubation. On the other hand, nitrate was only detected at the two highest concentrations tested. Initial observations of these enrichments indicated that as sulfide disappeared the brine turned from a transparent yellow color to a yellowish-white, cloudy suspension. Eventually the suspension settled to the bottom of the bottle leaving a clear, colorless liquid. Analysis of the particulate fraction revealed the presence of elemental sulfur and calcite crystals. Examination of the soluble fraction did not reveal an increase in either sulfate or sulfite; instead, analysis of total soluble sulfur (TSS) by x-ray fluorescence indicated a 1.5 mM decrease in soluble sulfur consistent with formation of elemental sulfur. The TSS represents only 41% of the HS^- oxidized suggesting that other forms of soluble sulfur remained undetected or that the TSS method was not quantitative. We suspect the latter since it is not likely that other unmeasured species of soluble sulfur (e.g., thiosulfate, polythionates) would form stable end-products. The only detectable nitrogen end-products were nitrite and dinitrogen gas. Nitrogen gas was determined to be an end-product by spiking enrichments with 5 mM ^{15}N-nitrate and confirming the presence of ^{15}N-labeled nitrogen gas. No ^{15}N-labeled N_2O or NO were detected and no $^{15}N_2$ was detected in headspace of control bottles without either indigenous bacteria or nitrate.

Accordingly the following stoichiometry is presumed for the Coleville enrichments:

$$5\,HS^- + 2\,NO_3^- + 7\,H^+ \rightarrow 5\,S_o + N_2 + 6\,H_2O$$

The stoichiometry is based on the quantitative analysis of nitrate and sulfide and the confirmation of elemental sulfur and N_2. Nitrite was excluded as an end-product since in the absence of excess nitrate (i.e., 1.5mM), nitrite did not accumulate (Table 1). This reaction stoichiometry differs from that for the sulfide bioscavenger *Thiobacillus denitrificans* in which sulfide is oxidized completely to sulfate:

$$5\,HS^- + 8\,NO_3^- + 3\,H^+ \rightarrow 5\,SO_4^= + 4\,N_2 + 4\,H_2O$$

This reaction requires four times more nitrate per mole of sulfide oxidized indicating that this reaction is less effective than the Coleville enrichment reaction. Also the increase in ionic strength caused by the production of sulfate is known to be inhibitory (8). On the other hand, elemental sulfur formed in the former

reaction, can be corrosive and can cause potential injectivity problems; however, it is anticipated that much of the elemental sulfur formed will dissolve in the oil and be carried out of the system.

Kinetics and Efficiency of Sulfide Oxidation in Porous Media

The results in Table 2 indicate that the injection of 5 PV of neat, unfiltered Coleville brine resulted in uniform concentrations of sulfide across the core. The subsequent addition of 5 mM KNO_3 and 100 μM KH_2PO_4 however, resulted in complete disappearance of sulfide in the outlet, but only after a shut-in period of approximately 3 days. SRB and NRB bottle counts sampled prior to shut-in indicated bottle counts 2-3 orders of magnitude higher in the inlet vs. the outlet, suggesting that convective transport of these bacteria through the core was not very efficient. Following shut-in, however, bottle counts of SRB and NRB increased significantly at the outlet. An increase in NRB was expected, as these bacteria are responsible for sulfide removal; whereas, the increase in SRB was not expected. Prior laboratory tests using brine enrichments and field tests had indicated that NRB, but not SRB, increased upon addition of nitrate to the brine (6). Nevertheless, the data support the fact that biological and not abiological factors were responsible for the removal of sulfide.

By the 20th PV, it appeared that a stable microbial population had been established in the core at a flow rate of 0.1 cc/min, as evidenced by the absence of injected sulfide at the outlet. At this point, the flow rate was increased to 1.0 cc/min and filtered brine without nutrients was injected, to re-establish outlet sulfide concentrations. Interestingly, the sulfide levels at the outlet did not reach inlet concentrations for almost 7 pore volumes (Figure 3), which suggested that residual oxidizing activity remained following termination of nitrate injection. Once the inlet and outlet sulfide concentration were equal, nutrients were again injected into the core. The sulfide concentration began to decrease at the outlet within the first PV of nutrients injected, and after about 6 PV of injected brine the outlet sulfide concentration had dropped from 53 mg/l to approximately 20 mg/L. A decrease in the flow rate from 1.0 to 0.5 cc/min resulted in an 87% reduction in sulfide across the core (PV 36.5, fig. 2). The core was then shut-in for 28 days until more brine was received from the field. Upon re-injection of brine, the outlet sulfide concentration, again, did not reach inlet levels for a delayed period, this time for about 4 pore volumes (PV 37-41, fig. 2). Possibly, some other mechanism of sulfide scavenging associated with the biofilm is occurring in the absence of nitrate. Once outlet concentrations of sulfide were re-established, injection of filtered brine containing nitrate and phosphate resulted in complete oxidation of the 43 mg/L sulfide injected within 2 PV. Complete oxidation of inlet sulfide was still apparent when the flow was increased to 1.0 cc/min; however, increasing the flow rate to 2.0 cc/min resulted in detectable amounts of sulfide (7 mg/L) in the outlet. (PV 43-54, fig. 2).

The efficiency of sulfide oxidation and oxidation rates were calculated for the core both before and after the 28 day shut-in. Before the shut-in, oxidation rates were 0.92 and 0.87 at HRTs of 0.75 and 1.5 hr, respectively, with sulfide oxidation

efficiencies of less than 90%. Following shut-in, sulfide oxidation efficiencies increased to 100% at both flow rates and at a HRT of 0.75 hr (i.e., 1.0 cc/min), the rate increased from 0.92 to at least 2.4 mmol sulfide/L/h, suggesting that optimal sulfide oxidation conditions within the core were still not established. Increasing the flow rate to 2.0 cc/min (HRT=0.38 hr) resulted in a maximal oxidation rate of 3.9 mmol sulfide/L/h, at an efficiency of 88%. Reported H_2S oxidation rates measured in other bioreactors using various sulfide-oxidizing bacteria range from 0.09 - 3.8 mmol sulfide/L/h (9). Therefore, the rates measured here compare very favorable with those measured elsewhere. In general, the ratio of HS^- oxidized per nitrate reduced decreased following the shut-in, indicating it was taking more nitrate to oxidize the same amount of sulfide. Perhaps a different biofilm had established and competition by non-sulfide-oxidizing NRBs for nitrate was occurring or the reduction of nitrite had become rate-limiting in the presence of excess nitrate. Molar concentrations of nitrite in the effluent were nearly equal to the molar concentrations of sulfide being injected, suggesting that nitrite was not being further reduced and was likely rate limiting. Nitrite did not accumulate in batch culture reactions in the absence of excess nitrate, implying that if sufficient time is allowed, nitrite will be reduced as well. This would likely be the case in the Coleville reservoir, as retention times are generally on the order of days or longer.

The production of elemental sulfur, bacteria, and calcite could present a problem in terms of reductions in injectivity and reservoir plugging. Morris et al(10), reported reductions in permeability in a laboratory core system injected with sour water from a gas storage reservoir amended with nitrate and attributed this reduction to increased levels of slime-producing denitrifiers. On the other hand, McInerney et al.(11) did not observe a significant loss of injectivity in core experiments that they conducted using *Thiobacillus denitrificans* strain F for remediation of sulfide from formation waters. The cause for these discrepancies could be a differences in the permeability of the cores, however, no information regarding permeability was given in the reports. Also, strain F is known to produce sulfate, and not sulfur as an end-product of sulfide oxidation, which would not be expected to contribute to injectivity loss. Our results indicate that there were no significant permeability changes across the core following all treatments (results not shown). The ceramic cores used in our study have a relatively high permeability of about 1 - 2 Darcy which is close to the average permeability of the Coleville reservoir. The formation of calcite observed in the enrichments is likely due to an increase in pH associated with the degassing of CO_2 in the brine at atmospheric pressure. The pH of Coleville injection brine measured in the field at reservoir pressure is approximately 7.3.

Sulfide oxidation rates, sulfide removal efficiencies, reaction stoichiometry, and core injectivity results suggest that bioscavenging of injected sulfide can be effectively carried out by the indigenous sulfide-oxidizing NRB found in the Coleville brine at the retention times likely to be present in the reservoir. Due to the oxidative nature of this process questions remain concerning the effects of this scavenging process on corrosion. Also, the potential effects of sulfur-reducing bacteria and other bacteria on the reversal of this reaction, especially in the absence

of sulfide and presence of hydrocarbons, along with residual sulfate in the reservoir, is unknown. We have found that biogenic sulfide can be regenerated in Coleville enrichments upon addition of acetate (results not shown).

Voordouw et al.(12) recently reported on the isolation of a novel sulfide-oxidizing NRB from the Coleville brine which they identified as a *Camplyobacter* sp. They reported the presence of this bacterium in other western Canadian oil-field waters and suggested that it is a vital link in the cycling of sulfur in these oil reservoirs. They also warn that additional injection of nitrate may lead to an undesirable boost in oil field microbial activity. The results in this paper suggest that there are other bacteria (i.e., non sulfide-oxidizing NRB) in the Coleville brine capable of competing for nitrate. Further laboratory and field tests should help to answer these concerns and others regarding the use of indigenous NRB as effective sulfide bioscavengers in oil field reservoirs.

REFERENCES CITED

1. Kalpacki, B., Magri, N.F., Ravenscroft, P.D. , McTeir, M.D.K. and Arf, G.T. "Mitigation of Reservoir Souring - Decision Process," (SPE 28947) presented at the SPE International Symposium on Oilfield Chemistry, San Antonio, TX, February 14-17, 1995.
2. Jenneman, G.E., McInerney, M.J. and Knapp, R.M., "Effect of Nitrate on Biogenic Sulfide Production," *J. Appl. and Environ. Microbiol.* 51, 1205-1211 (1986).
3. Sandbeck, K.A. and Hitzman, D.O., "Biocompetitive Exclusion Technology: A Field System to Control Reservoir Souring and Increase Production," in proceedings of the Fifth International Conference on Microbial Enhanced Oil Recovery and Related Biotechnology for Solving Environmental Problems, Richardson, TX, 1995.
4. Sublette, K.L., Morse, D.E. and Raterman, K.T. "A Field Treatment of Sour Produced Water Remediation by Microbial Treatment," (SPE 26396) presented at the SPE Annual Technical Conference, Houston, TX, October 3-6, 1993.
5. McInerney, M.J., Sublette, K.L., Bhuparthiaraju, V.K., Coates, J.D. and Knapp, R.M. "Causes and Control of Microbially Induced Souring," *Developments in Industrial Microbiology - Recent Advances* 39, 363-371 (1993).
6. Gevertz, G., Jenneman, G.E., Zimmerman, S. and Stevens, J., "Microbial Oxidation of Produced Water from the Bakken Sands", in proceedings of the Fifth International Conference on Microbial Enhanced Oil Recovery and Related Biotechnology for Solving Environmental Problems, Richardson, TX, 1995.
7. Fogo, J.K. and Popowski, M., "Spectrophotometric Determination of Hydrogen Sulfide," *Analytical Biochemistry* 21, 732-734 (1949).

8. Ongcharit, C., Sublette, K. L. and Shah, Y. T., "Oxidation of Hydrogen Sulfide by Flocculated Thiobacillus denitrificans in a Continuous Culture," Biotech Bioeng. 37, 497-504 (1991).
9. Jensen, A. B. and Webb C., "Treatment of H_2S-containing gases: A review of Microbial Alternatives," *Enzyme and Microbial Technology* 17, 2-10 (1995).
10. Morris, E.A., Kenny, T.M. and Pope, D.H., "Field and Laboratory Tests on Nitrate Treatment for Potential Use in Natural Gas Operations," (SPE 029738) presented at the SPE/DOE Exploration and Production Environmental Conference," Houston, TX, March 27-29, 1995.
11. McInerney, M.J., Wofford, N.Q., and Sublette, K.L., "Microbial Control of Hydrogen Sulfide Production in a Porous Medium," *Applied Biochemistry and Biotechnology* 57/58, 933-944 (1996).
12. Voordouw, G., Armstrong, S.M., Reimer, M.F., Fouts, B., Telang, A.J., Shen, Y. and Gevertz, D., "Characterization of 16S rRNA Genes from Oil Field Microbial Communities Indicates the Presence of a Variety of Sulfate-Reducing, Fermentative, and Sulfide-Oxidizing Bacteria," *J. Applied and Environmental Microbiology* 62, 1623-1629 (1996).

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Table 1

Nitrogen and sulfur products formed following bio-oxidation of sour injection brine by Indigenous NRB in a Coleville enrichment.

Nitrate (mM)	Reactants (mM)		Nitrogen End -products [a] (mM)						Sulfur End-products [b] (mM)				
	$[HS^-]_{ox}$	$[NO_3]_{red}$	$[NO_3]$	$[NO_2]$	$[NH_4^+]$	N_2O	NO	N_2	$[HS^-]$	$[SO_4^{-2}]$	$[SO_3]$	TSS [c]	So [d]
0	0.0	0.0	0.0	0.0	0.0	-	-	-	4.2	- 0.2	0.0	ND	-
0.7	1.4	0.7	0.0	0.0	ND	ND	ND	ND	1.7	ND	ND	ND	ND
1.5	3.3	1.5	0.0	0.0	0.0	ND	ND	ND	0.0	ND	ND	ND	ND
2.1	3.2	1.9	0.3	0.5	ND	ND	ND	ND	0.0	ND	ND	ND	ND
5.6	3.4	1.8	3.8	0.4	0.0	-	-	+	0.0	- 0.5	0.0	- 1.5	+

[a], gaseous nitrogen products were determined from an independent experiment using GC/MS analysis of ^{15}N-labeled head space gases (see methods); [b], soluble sulfur products were determined from an independent experiment in which initial $[HS^-]$ = 3.7 mM; [c], total soluble sulfur by x-ray fluorescence; [d], presence of elemental sulfur confirmed by scanning electron microscopy and electron dispersion spectroscopy of precipitates; +, present; -, absent; ND, not determined.

Table 2

Results of the inoculation and pre-treatment of ceramic core with Coleville brine and inorganic nutrients.

Treatment	Q cc/min	PV [c]	Sulfide ppm			SRB		NRB	
			Res [a]	In	Out	In	Out	In	Out
Unfiltered CVU brine	1.0	5	64	52	52	3	1	6	2
Filtered CVU brine + NO_3^-/PO_4^{-3} [b]	1.0	10	ND	52	52	4	2	4	2
Shut-in 2.8 days	0.0	NA	ND	ND	0	ND	ND	ND	ND
Filtered CVU brine + NO_3^-/PO_4^{-3} [b]	1.0	13	64	40	28	ND	ND	ND	ND
CVU synthetic brine	1.0	14	ND	ND	18	ND	ND	ND	ND
Filtered CVU brine + NO_3^-/PO_4^{-3} [b]	0.1	15.3	ND	40	0	3	5	6	5
Filtered CVU brine + NO_3^-/PO_4^{-3} [b]	0.1	20.2	ND	24	0	4	ND	8	ND
Filtered CVU brine	1.0	23.8	ND	ND	16	ND	5	ND	6

[a], Reservoir; [b], 5.0 mM KNO_3 + 100 uM KH_2PO_4; [c], Cumulative pore volumes; ND, not determined

Table 3

Results of the injection of nitrate and phosphate[a] on the oxidation of sulfide in a ceramic core containing sulfide-oxidizing NRB present in Coleville brine.

Date	n	$[HS^-]_{in}$ mM	$[HS^-]_{ox}$ mM	$[NO_3^-]_{red}$ mM	$[HS^-]_{ox}/[NO_3^-]_{red}$	$[NO_2^-]$ mM	V ft/d	HRT* hr	Oxidation rate mmol/L/h	Oxidation efficiency (%)
12/15/95	7	1.6 (.19)	.69 (.35)	.50 (.16)[b]	1.4	0.0 - 1.0	31	0.75	0.92	43
12/15/95	3	1.5 (0.0)	1.3 (.10)	0.63	2.1	1.4	16	1.5	0.87	87
1/12/96	7	1.3 (.24)	1.3 (.22)	1.4	.93	2.3	16	1.5	0.87	100
1/12/96	4	1.8 (.36)	1.8 (.36)	1.6 (.88)[b]	1.1	2.3	31	0.75	2.4	100
1/12/96	4	1.7 (.28)	1.5 (.27)	1.6	.94	1.7	62	0.38	3.9	88

[a], 5 mM KNO_3 + 100 μM KH_2PO_4 [b], n = 2 ( ), Standard Deviation *, HRT, hydraulic retention time based on the volume between inlet and outlet sample port.

CORE FLOOD SYSTEM

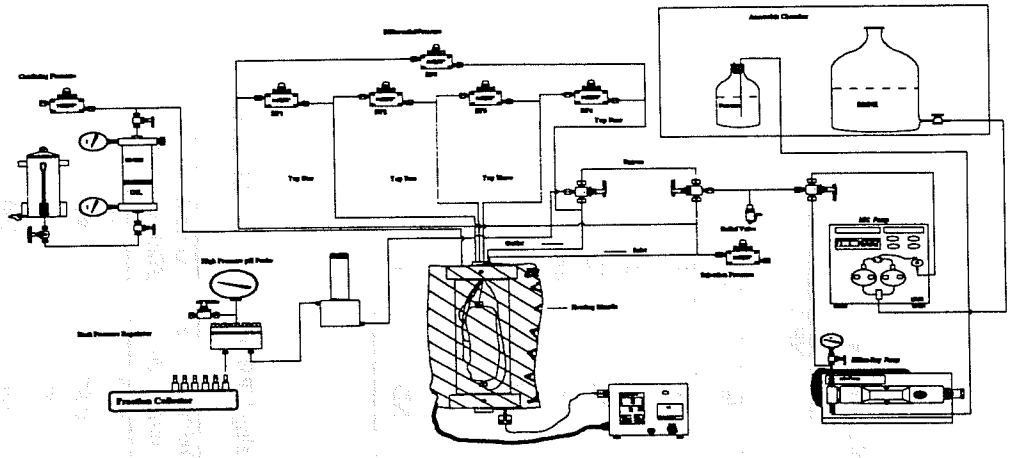

Figure 1. Coreflood apparatus

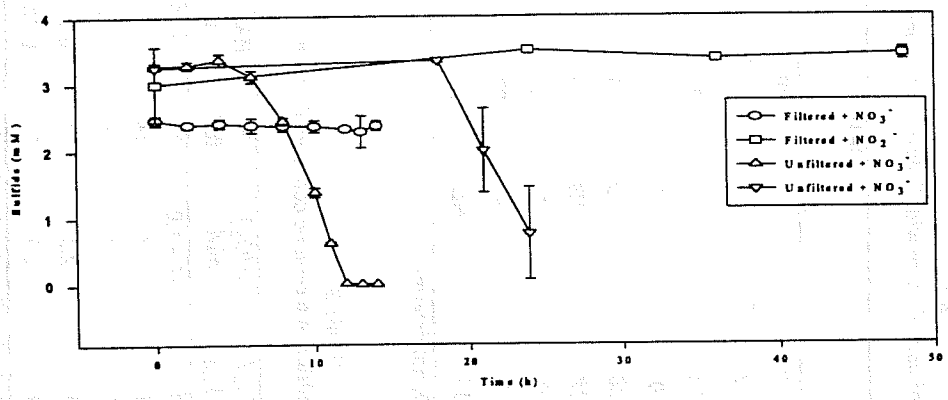

Figure 2. Kinetics of NO_3^-/NO_2^- addition on rates of sulfide bioscavenging in filtered and unfiltered brine.

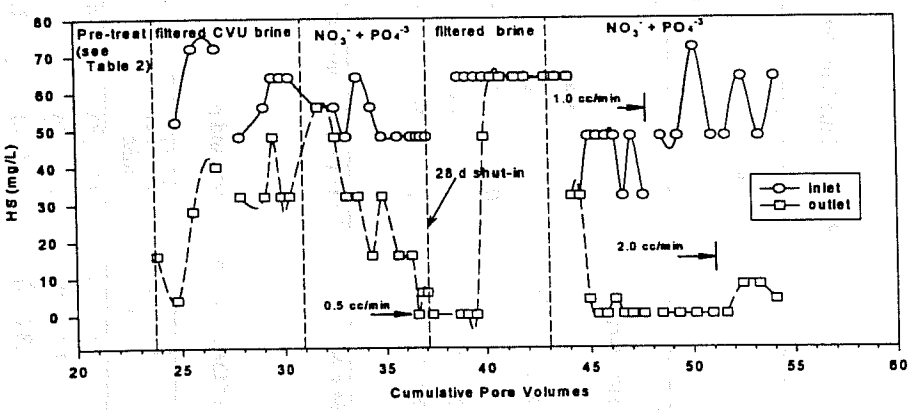

Figure 3. Kinetics of sulfide scavenging in a ceramic core inoculated with indigenous Coleville bacteria.

DEVELOPMENT OF A NOVEL BIOLOGICAL CATALYST FOR DESULFURIZING THE SOUR NATURAL GAS

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ABSTRACT

A novel biological process, BIODESULF™ (patent pending), developed at ARCTECH removes H_2S and other sulfur contaminants that make the Natural Gas Sour. In this process, in the temperature range of 50°F to 140°F, pH range of 7.5-8 and at a pressure of 1,000 psi; carbon dioxide, carbonyl sulfide, hydrogen sulfide and mercaptans (dimethyl, ethyl and methyl) are removed to pipeline specifications. The rate of conversion to elemental sulfur is 1.0 lb/ft^3h^{-1}, which is ten fold higher than that obtained from conventional scavenger technologies. The H_2S is removed from 10,000 ppm concentration to $\leq$4 ppm. Independent studies indicate that for processing 1TPD sulfur, the BIODESULF'™ Process uses 6.7 fold less catalyst than that used in the ARI- LO-CAT™ process and 16.7 less than the BIO-SR™ Process. BIODESULF™ process is cost-effective in contrast to state-of-the-art technologies.

INTRODUCTION

Estimates are that up to 15% of the present Natural Gas production in the United States are sour and up to 78 TCF or 14% of U.S. Natural Gas reserves are also sour[4]. By the year 2,000 the Sour Natural Gas (SNG) production is estimated to be at the rate of 3-6 TCF/ year. This souring is due to the presence of sulfur compounds, principally hydrogen sulfide (H_2S) in the SNG. The other sulfur contaminants are: carbonyl sulfide (COS), carbon disulfide (CS_2) and mercaptans - dimethyl ($[CH_3]_2S$), ethyl (C_2H_5SH) and methyl (CH_3SH). Among these contaminants, H_2S is an acid gas that is toxic and corrosive, especially in presence of moisture.

A significant portion of the total Natural Gas produced does not meet the pipeline standards and needs treatment to reduce the H_2S concentration to ¼ grain per 100 standard cubic feet (SCF), or ~ 4-6 mg/ L, or < 4 ppmv[17]. The other sulfur compounds listed above are present in up to 0.2% concentration or 2,000 ppm and should be reduced to < 1,000 ppm. The state-of-the-art technologies[8-10] to remove the H_2S from the SNG are:

- Amine/ Claus Process
- Liquid Redox Processes
- Scavenger Technologies

Amine Process

In the Amine Process, the SNG stream is contacted with the amine solvent to remove the H_2S. The solvent is subsequently regenerated by heating to 194° F to 302°F (90°C to 150°C) when the H_2S is liberated and thus the H_2S is not mitigated. Thus liberated H_2S can either be incinerated, whereby it will liberate SO_2, which adds to the air pollution. A preferred alternative method is to physicochemically treat the H_2S in the Claus Process[14,17]. In this process, the H_2S is fed into the reaction furnace and passed through a series of catalytic converters to transform the H_2S to elemental sulfur. Although, high quality sulfur is produced, the Claus Process is often too expensive for small capacity producers, i.e. those producing ≤ 2 million standard cubic feet per day (<2 MMSCFD) of Natural Gas.

Liquid Redox Processes

The alternative process is the Liquid Redox Process. The Liquid Redox processes have recently been reviewed[4]. In the Liquid Redox processes (Technologies), the catalysts are chelated iron or vanadium, mostly iron in the ferric form. These catalysts, in combination with other sulfur mitigation and recovery processes have widely been used during last three decades. The chemistry of this process can be simply shown by the chemical equation:

$$H_2S + 2Fe^{+3} \rightarrow S + 2H^{+1} + 3Fe^{+2} \quad \text{.....Eqn.1}$$

$$\tfrac{1}{2}O_2 + 2Fe^{+2} + 2H^{+1} \rightarrow 2Fe^{+3} + H_2O \quad \text{.....Eqn. 2}$$

Thus, the overall equation can be written as follows:

$$H_2S + \tfrac{1}{2}O_2 \rightarrow S + H_2O \quad \text{.....Eqn. 3}$$

Mr. Derek McManus, in another technical paper[12] in this volume provides an excellent review and recent modifications made to liquid redox catalysts, specially ARI-LO-CAT II™. Nevertheless, the limitations of the liquid redox processes are high costs and the difficulty of regenerating the sulfide mitigation catalysts which are used, degenerated and reduced during the process of H_2S mitigation and conversion to elemental sulfur. According to another report[3], other difficulties encountered with these processes are:

1. catalyst poisoning,
2. operational difficulties, such as foaming and the equipment corrosion,
3. reduced process efficiency, and
4. economic limitations.

McManus[12], however, points out that some of these difficulties have now been resolved by better understanding the chemistry of the liquid redox catalyst and also the newer generation of catalysts.

Scavenger Processes

The scavenger processes involve only one time throughput and are considered to be cheaper in comparison to other state-of-the-art technologies. In these processes, the scavenger, in either liquid or the solid form is loaded into an appropriate reactor. The SNG is either passed over the catalyst (if solid), or is bubbled through the reactor. During this passage, the H_2S is adsorbed to the liquid or the solid catalyst and is usually oxidized to SO_4^{-2} which is then disposed off[9]. Nevertheless, similar to Liquid Redox technologies, the Scavenging Processes also have limitations. These limitations are:

1. foaming,
2. equipment fouling, and
3. applicability to treat only up to 0.1lb/ft^{3}hr^{-1} of sulfur as H_2S.

Besides, the operational and economical problems associated with each of the above described state-of-the-art technologies[3,4,8-10,14], the Natural Gas Procesing Industry is faced with increasing stringent environmental regulations. Thus, the industry seeks an alternative SNG processing technology that is:

- operator friendly,
- cost effective,
- production size based, and
- can be easily adapted to the field conditions.

Review of the recent literature indicates that in contrast to chemical or physicochemical processes, the biological processes offer three distinctive advantages. First of all, the biological processes can be operated at near ambient conditions of temperature and pressure. Secondly, these processes are much more specific in terms of attacking a particular contaminant because the reactions, albeit, conceivably take place at a lower rate, are enzyme specific and lead to a specific by product stream. A third advantage of the biological processes is that the catalysts (biocatalysts, i.e. microorganisms) that carry out the reation rates are self-regenerating. Thus, in contrast to Amine or Liquid Redox processes, a separate reactor is not required to regenerate the catalysts. Because of these reasons, the biological processes can be potentially cost-effective in contrast to their physicochemical counterparts. The biological processes, however, can not handle the volumes of SNG that are treated by the Amine Processes, nevertheless, the former processes are more suitable for the marginal or tail gases being produced at ≤ 2MMSCFD.

In recent years several microbiological processes have been investigated that utilize chemoaotutrophic bacteria[5,10,16&17]. These bacteria, belonging to Genus *Thiobacillus*[2] are used in two ways. In the first type of reaction, the *Thiobacillus ferrooxidans* regenerates the iron through the oxidation of Fe^{+2} to Fe^{+3} when the Liquid Redox catalyst is regenerated (BIO-SR™ Process)[16] according to the chemical reactions 4 and 5.

$$H_2S + Fe_2(SO_4)_3 \rightarrow S\downarrow + 2FeSO4 + H_2SO_4 \quad \text{..... Eqn.4}$$

$$FeSO4 + H_2SO_4 + {}^{1}/_{2}\, O_2 \xrightarrow{T.ferrooxidans} Fe_2(SO_4)_3 + H_2O \quad \text{... ..... Eqn.5}$$

In the direct treat biological processes, however, the bacteria of the Genus *Thiobacillus* oxidize the sulfide species by using them as a source of energy in the presence of CO_2 or HCO_3^{-1} as the carbon source, and NH_4^{+1} or NO_3^{-1} as the source of nitrogen[2], according to the chemical equation 6.

$$0.422H_2S + 0.422HS^{-1} + NO_3^{-1} + 0.346\, CO_2 + 0.0685\, HCO_3^{-1} + 0.0865\, NH_4^{+1} \rightarrow$$
$$0.844\, SO_4^{-2} + 0.5\, N_2 + 0.288\, H^{+1} + 0.4025\, H_2O + 0.0865\, C_5H_7O_2N \text{ (biomass)} \text{.....Eqn.6}$$

Literature shows that in contrast to a homogeneous culture consisting of only one bacterial species, a mixed culture, such as a bacterial or microbial consortium consisting of different morpho- and physiotypes of bacteria/ microorganisms, brings about 75% higher sulfide oxidation than that catalyzed by a chemical agent. The important condition, however, is that the sulfide concentration should be ≤ 3

Literature shows that in contrast to a homogeneous culture consisting of only one bacterial species, a mixed culture, such as a bacterial or microbial consortium consisting of different morpho- and physiotypes of bacteria/ microorganisms, brings about 75% higher sulfide oxidation than that catalyzed by a chemical agent. The important condition, however, is that the sulfide concentration should be ≤ 3 mM and reaction conditions should be favorable for the microbial metabolism[Cf.17] . With these considerations, the objectives for the development of the BIODESULF`™ process (patent pending) were to develop a biological process for the sweetening of SNG which:

- meets pipeline specifications (`≤ 4 ppm H_2S and regulatory limits for other sulfur species, such as COS, CS_2, CH_3SH, $[CH_3]_2SH$, C_2H_5SH, and CO_2),
- achieves specific sulfur removal rates of at least 0.1 lb/ft^3h^{-1}
- is applicable for small scale operations (~0.2 to 2 TPD of sulfur), and
- reduces costs for desouring the SNG.

The results presented in the present paper clearly demonstrate that the BIODESULF™ Process meets all of the above criteria. Thus, on a bench scale, the technical feasibility of a cost-effective, direct treat biological catalyst (biocatalyst) and a biological process for the sweetening of SNG is established.

MATERIALS AND METHODS

Microorganisms, chemicals, methods and the equipment used in the development of the BIODESULF™ Process (Patent pending) are detailed below.

A. Materials

The materials used were: bacterial/microbial cultures, chemicals and reagents, specialty gases, and culture media to cultivate the microorganisms.

a. **Bacterial /Microbial Cultures** Two types of bacterial cultures were evaluated in the initial work. The first group consisted of three bacterial consortia (group of bacteria belonging to different morphotypes and physiotypes) from the ARCTECH Microbial Culture Collection (AMCC) called SSI, SSII and AMDI. The second group consisted of a strain of *Thiobacillus denitrificans* (TD) and a culture of *T. ferrooxidans* (TF), obtained from the American Type Culture Collection (ATCC). The TD and the TF were included in preliminary studies for comparative purposes only.

b. **Chemicals And Reagents** All chemicals and reagents used were purchased from Sigma Chemical Co., VWR Scientific Co., or Fisher Scientific Co. The organic nitrogen amendment, Sheftone-T™ and Cargill 200/20, were ordered from Sheffields Products Co, NY and a private vendor respectively.

c. **Specialty Gases** Carbon dioxide, compressed breathing air, hydrogen, helium, nitrogen, simulated Sour Natural Gas (SSNG) and the 10,000 ppm H_2S standard were obtained from Air Products, Allantown, PA. The H_2S standard of 4 ppm was obtained from the Scotts Specialty gases, PA. The SSNG was of two different composition. Unless otherwise indicated, the

SSNG contained either 200 or 10,000 ppm H_2S, mixed with 0.1% to 0.2% of each of COS, CS_2, CH_3SH, $[CH_3]_2S$, and C_2H_5SH, 5 to 10% C_{O2}, 5% N_2 and balance methane (CH_4).

d. **Culture Media to Cultivate Microorganisms** Initial growth screening tests for all microbial cultures (consortia from AMCC as well as TD and TF from ATCC) and all evaluation tests for the capability of the test organisms for mitigating H_2S was carried out in the TDM described in the ATCC manual. For the remaining studies on the development of BIODESULF™ process, a more cost effective, proprietary culture medium, CSTDM was developed at ARCTECH. The composition of CSTDM is based on TDM, but several of the TDM components are either modified or omitted. Thus, CSTDM is >95% cost effective than TDM, without compromising the microbial growth or metabolism.

B. Methods

The experimental procedures used for evaluating the process parameters for the BIODESULF™ process are described below.

a. **General Experimental Procedures** Initially, all experimental procedures to handle the microbial cultures (consortia, TD or the TF) were carried out under anaerobic conditions according to the techniques described by Hungate[7] as modified by Bryant[2]. An anaerobic glove box (Coy Corporation, Ann Arbor, MI) was used for culture transfers, cell washing, and isolation of cell types for various microbial consortia. In the glove box, anaerobic conditions were maintained with an oxygen-free mixture of N_2 + H_2 (90:10). The anaerobic conditions during media preparation and in the reaction vessels, were maintained by bubbling an oxygen-free mixture of N_2 + CO_2 (80:20). For these experiments, all solutions, reagents and culture media were prepared under the same anaerobic conditions. Microbioreactors (Serum vials) of 125-mL containing 60mL of culture medium were used for all preliminary experiments, and Wheaton bottles (1-L) were used for growing the microbial inocula. The initial pH of the culture medium was adjusted to 7.5. The vials were stoppered with butyl rubber stoppers and aluminum crimp sealed. The Wheaton bottles used to grow larger quantities of microbial inocula were stoppered with butyl rubber stoppers and screw capped.

For any given experiment, in any type of reactor and either during the laboratory scale, bench scale, or for the process research, the headspace gas was sampled at periodic intervals (5 minutes to 4 hours to at least once every 24 hours) with a gas tight syringe. Headspace is the space between the bottom of the cover (butyl rubber stopper for microbioreactors, stainless steel flange cover for the bioflow and Parr reactor) of a reactor, and the top of the liquid meniscus in the reactor. During preliminary experiments, liquid samples were also aseptically and anaerobically removed for analysis of pH, cellular protein (to measure the cell growth) and estimation of soluble sulfur species: elemental sulfur (S_o), SO_3^{-2}, SO_4^{-2}, $S_2O_3^{-2}$ and S^{-2}.

The above procedures were used because originally the SSII and other AMCC consortia were developed under anaerobic conditions. Since anaerobic cultures require special attention and techniques, an experiment was set up to determine whether the SSII consortium, which showed highest mitigation of sulfur species from the SSNG, is a facultaive or obligate anaerobe. The results from this experiment confirmed that the SSII consortium is constituted

of microaerophilic or facultative anaerobic microorganisms. Therefore, the cultures were treated in the ambient conditions, and anaerobic methods were not followed to either cultivate or maintain the SSII consortium.

b. **Inoculum Preparation** For initial screening experiments to select which of he five microbes, the consortia (SSI, SSII, AMD1), TD and TF gave the highest mitigation of the sulfur species form the SSNG, the innocula were prepared in 1-L Wheaton bottles containing 300 mL of the TDM medium. After an incubation period of one week, the cultures were aseptically and anaerobically harvested by centrifugation and washed twice in equivalent quantity (200 mL) of 50 mM, pH 7.5 Tris-HCl buffer, by re-suspension and centrifugation. Finally, the washed microbial pellet was re-suspended in sufficient culture medium (CSTDM) to provide enough inoculum for the experiment to be performed. Initial screening experiments were carried out at the microbial loading of 1% Inoculum (v/v). The wet weight of the inoculum was recorded and the total cell count measured directly with epifluorescence microscopy[6]. This method of inoculum monitoring provided a means of keeping the initial bacterial inoculum constant for different treatments within a given experiment or between the experiments. It also provided a method whereby all the four bacterial cultures were tested at the same microbial load. Thus, any discrepancy due to bacterial numbers or variations in the microbial loading could be disregarded or minimized.

Larger quantities of inoculum required for the scaled up experiments at the bench and process research experiments that were conducted in the Bioflow and in the Parr Pressure reactors respectively. Therefore, for these experiments, the inoculum was prepared in 4-L Erlenmeyer flasks containing 2 L CSTDM prepared with sodium citrate trihydrate. The sodium citrate was used to get rapid growth of the SSII microbial consortium. After appropriate period of incubation, the biomass was harvested through centrifugation washed with Tris-HCl buffer (pH 7.5, 20 mM) for two passages and resuspended at appropriate biomass loading , 2.1 G • $600mL^{-1}$ to 60 G • $600mL^{-1}$, depending upon the experiment to be conducted and the reactor to be used for that experiment.

c. **Analytical Methods** Analysis of the headspace samples was by gas chromatography and those of soluble sulfur species by high pressure liquid chromatography (HPLC) and/or gravimetry. The microbial load and the growth was determined either by direct cell count, measuring the absorbance at 460 nm (OD_{460}), or by wet and dry cell weight.

The wet cell weight was determined on a 24-48 hr culture of the test organism. The culture was dispensed in a pre-weighed centrifuge bottle of 50- to 250-mL. The culture was harvested through centrifugation at 3,000 to 3,500 rpm for 20 minutes. Subsequently the cell pellet was, atleast twice, washed with Tris-HCl buffer (20 mM, pH 7.5) through resuspension and centrifugation. Finally, the centrifuge bottle containing the cell pellet was weighed. For determining the dry cell weight, the cell pellet after determining the wet weight was resuspended in 50 mL of Tris-HCl buffer (20 mM, pH 7.5) and transferred to a pre-weighed aluminum boat. Three such preparation were used for this determination. In 3 other pre-weighed boats, 50 mL Tris-HCl (20 mM, pH 7.5) was dispensed into each one. These three boats served as controls. All the six boats were then dried for 16 hr at 105°C. Subsequently,

the boats were cooled in a dessicator and weighed until a constant weight was obtained. The wet weight (wwt) was obtained as :

wwt = A - B,

where A is the weight of harvested, washed cell pellet + the pre-weighed centrifuge bottle, and

B is the weight of the centrifuge bottle.

Similarly, the dry weight (dwt) was calculated from the formula:

dwt = C-D-E,

where C is the weight of the dried, pre-weighed aluminum boats containing 50 mL of the washed culture suspension in Tris-HCl buffer,

D is the weight of the dried, pre-weighed aluminum boats containing 50 mL of the Tris-HCl buffer, and

E is the weight of the aluminum boat alone.

The parameters used for HPLC were: a Waters 501 HPLC pump connected to a WISP U6K autosampler. The column was an IC-PAK A HC 150 X 4.6 mm connected to a 400 UV detector at 220 nm. In series with the UV detector was connected a 430 conductivity detector and the latter detector's effluent line was connected to a waste stream jug. The eluent was, 5mM dibasic sodium phosphate with a flow rate of 2 mL• min^{-1}. The eluent was prepared by adding 0.7092 g dibasic sodium phosphate (Na_2HPO_4) to a 1-L volumetric flask and bringing the volume to the mark with HPLC grade water. The eluent was filtered through a 0.2μm membrane filter and protected from adsorbing atmospheric CO_2 by using a column of ascarite.

Standard solutions were prepared by diluting to 100 mL (Table 1) in a 100-mL volumetric flask the concentrated solutions of each of the target sulfur species. The diluent was 20 mM dibasic sodium phosphate containing 10 mM mannitol. The concentrated standards were at 1,000 ppm, prepared by dissolving the following quantities of ACS grade sodium salts of each one of the target sulfur species. All weights are within 0.001 g of the weights indicated for each of the salts: S^{-2}, 0.749 g of $Na_2S.9H2O$; SO_4^{-2}, 0.148g of Na_2SO_4; SO_3^{-2}, 0.157 g Na_2SO_3 and $S_2O_3^{-2}$, 0.141 g $Na_2S_2O_3$.

The cell count was obtained by phase contrast or epifluorescence microscopy[21] using acrydine orange stain[6]. The OD_{460} of cultures was also measured as an indicator of the cell growth and was correlated with cellular protein concentration, wet cell weight and dry cell weight. The wet cell weight was determined by the modified protein BCA method[21].

d. **Determination Of Headspace Gases.** The headspace gas analyses were obtained by directly introducing the needle of a pressure-tight gas syringe into the butyl-rubber stoppers on the sample containers. For initial experiments in the microbioreactors, prior to sampling for headspace gas, the pressure-tight syringe was made anaerobic by flushing it three times with oxygen-free N_2+CO_2 mixture (80:20). For later experiments, however, this flushing step was not used because by now it was known that the SSII consortium is a facultative anaerobe/microaerophile.

Headspace gas composition for methane (CH_4), CO_2 and N_2 was determined by gas chromatography using a thermal conductivity detector (TCD). A GOW-MAC gas chromatograph (GC) fitted with a 10'x1/8" OD stainless steel column packed with 100/120 mesh Carboseive S-II (Supelco Co.) was used to analyze the gas samples. The conditions were: thermal conductivity (TC) detector ; column temperature, 200°C; detector and injector temperatures, 220°C; and detector current, 170mA. Helium was used as a carrier gas (34mL/min. at 50 psi on the cylinder). The data was integrated by an HP integrator (Model 3396A). The calibration standard was prepared with a mixture of carbon dioxide, CO_2 (29.3%); carbon monoxide, CO (10.2%); hydrogen, H_2 (4.9%); nitrogen, N_2 (24.9%); and methane, CH_4 (30.7%).

A Varian model 3700 Gas chromatograph was used for analyzing gaseous sulfur species. A flame photometric detector with sulfur filter at 220°C was used. The carrier gas was helium at a flow rate of 40 mL, min^{-1}. A 60/80 Carbopak B, 1.5% XE-60, 1% H_3PO_4 glass column was used. The oven temperature was isothermal at 50°C and the injector was set at 220°C.

e. Rate of Sulfur Species Removal The rate of removal of different sulfur species was calculated from the formula:

$R = dc \div dt$

Where,

R = rate of removal in $lbs \bullet ft^3\ hr^{-1}$

dc = change in the concentration (in lbs/ft^3) of sulfur species being tested, and

dt = time (in hrs) taken to change the concentration of sulfur species being tested

at equilibrium,

$R = C_i - C_o \div t$,

where C_i is the inlet concentration (in lbs/ft^3) for the sulfur species being tested,

C_o is the outlet concentration (in lbs/ft^3) of sulfur species being tested, and

t is the time (in hr) taken to reach equilibrium

C. Description Of The Equipment Used

The experiments described here were conducted in four types of reactors.

a. Microbioreactors Screening experiments were carried out in amber colored 125-mL microbioreactors (also known as serum vials) containing 60 mL of the TDM medium, then the microbioreactors were purged with O_2- free N_2 + CO_2 mixture (80:20 ratio) according to the methods of Hungate[7], as modified by Bryant[1]. Subsequmtly, the microbioreactors were stoppered with teflon coated butyl rubber stoppers and aluminum crimp sealed. A total of 36 microbioreactors were prepared in this manner. For each test microorganisms, a set of three microbioreactors was used. Thus, a set was for SSI, the next for SSII, a third for AMDI, the fourth for TD and the fifth for TF. The sixth set was for an abiotic control. All the 36 microbioreactors were autoclaved at 121°C and 15 psi for 25 minutes. After, autoclaving and

cooling, of the uninoculated microbioreactors, in sets of three microbioreactors to a set, a set was inoculated with a test microorganism as described in Table 2.

After inoculation, from each of the microbioreactor, 10 mL headspace gas (space between the liquid meniscus and the bottom of the teflon coated butyl rubber stopper) was withdrawn aseptically and anaerobically, and replaced with the same volume of SSNG contaiing 10,000 ppm H_2S, 10% CO_2 and balance N_2. Thus prepared microbioreactors were incubated for atleast 168 hours in a shaker Incubator (New Brunswick Scientific CO., mode I25G). maintained at 100 rpm and 37°C At periodic Intervals (4 hours to once every 24 hours), the microbioreactors were aseptically and anaerobically sampled for headspace gas composition and a liquid sample for the measurements of pH, cell growth and sulfur analysis.

b. **Equipment for Bench Scale Process Research at Atmospheric Pressure** The process research was carried out in three different reactors. Two of these, run at atmosperic pressure and at a temperature of 98°F (37°C), were obtained from the New Brunswick Scientific Company, New Jersey. The experimental set up for these experiments is presented in Figure 1. The reactor (10, either of 2-L or 14-L) was a glass jar with flanged top (11). The reactor was fitted with a stirrer 21 which was connected to a perforated shaft and the shaft was fitted with impellers (22) to allow the mixing when the reactor sat on the base (14). The stirrer (21) was connected to the SSNG line coming from a gas tank (12). The inlet gas flow from the tank to the reactor was regulated with the flow meter (16). In between the flow meter and the stirrer, the inlet line was fitted with a sampling port or inlet septum (24). This septum was used to sample the inlet gas for determining the inlet concentration of different components of the SSNG. Similarly, the reactor(10) was fitted with an outlet line (18) which was connected to a flask full of water (20) before the outlet gas was vented to a fume hood. A septum (26) was provided in the outlet line to allow for the sampling to determine the concentration of various components of the now desulfurized SSNG after it was treated with the biocatalyst (SSII microbial consortium culture).

c. **Equipment for Bench Scale Process Research at Higher than 1 Atmosphere Pressure** Further process research was conducted in a 1-L Parr pressure reactor according to the bench scale set up as presented in Figure 2. At 1,000 psi, either the SSNG containing 200 to 10,000 ppm H_2S, 5% CO_2 and 5% N_2 , or SSNG mixed with other SNG components and diluted with N_2 (if warranted by the experiment) was passed in a Parr pressure reactor through appropriate valves to control the flow of the inlet SSNG. Before the SSNG entered the Parr reactor, the composition of the SSNG was determined by sampling the gas through a port on the lid of the Parr reactor with a gas tight syringe as described earlier. The Parr pressure reactor was 1-L or a 2-L stainless steel jar containing 600 or 1200 mL CSTDM (in the pH range of 6.8 to 9.0 pH) with or without the biocatalyst. For abiotic controls, to establish whether the sulfur component removal from the SSNG was pH based or biocatalyst mediated, the SSII consortium was not suspended in the CSTDM. For experiments to evaluate the biological removal of sulfur species from the SSNG, the SSII microbial consortium was suspended in the CSTDM at different wet weight loadings ranging from 0.35% to 10% (2.1 G • $600mL^{-1}$ to 60 G • $600mL^{-1}$). The Parr Reactor assembly was fitted with an stirrer (D), a pressure gauge (E), and contained in a housing (F). The reactor temperature was controlled by controlling the housing temperature through a thermister connected to a

temperature controller. Alternatively, the temperature of the housing was also maintained in the range of 50°F (10°C) to 77°F (25°C) by recirculating cold water through a recirculating water bath maintained in the temperature range of 50°F(10°C) to 77°F (25°C). After, contacting with the biocatalyst, the SSNG passed through a flowmeter (G) and finally through an H_2S detector, J. The H_2S detector was calibrated with H_2S standards of 4 and 1,000 ppm and the values obtained from the detector were matched with those from the gas chromatograph analysis. The detector was specially useful for monitoring the gas composition during unattended hours as the data from the detector at any given hour was recorded on a videofilm through a videocamera (not shown in Figure 2). Thus, the experiments could be run by continuos passage of the SSNG through the reactor, or in semicontinous mode, when the gas flow was stopped for a pre-planned period, or even in the batch mode. During the day time, however, for the verification purposes, as well as to monitor the performance of the detector, in addition to recording the outlet gas composition from the detector, periodic samples were analyzed on the gas chromatograph as well. This practice also provided the requisite quality assurance and quality control of the data obtained through either mode of detection. For batch experiments, the reactor was charged with the SSII microbial consortium contained in the CSTDM medium, subsequently, the reactor was pressurized with the SSNG to be tested.

RESULTS AND DISCUSSION

The concept of biodesulfurization of sulfur containing gases including SNG or similar gases from other sources, such as landfill gas, was hypothesized on the basis of the chemical reactions 1 through 6 described in the Introduction section. In addition, a review of the pertinent literature[cf.17] indicated that a number of microbial species, specially *T. denitrificans* bioconverts mM quantities of H_2S. It was not clear, however, whether the reaction took place at atmospheric conditions or under those that are prevalent in the SNG Procesing. Therefore, the information presented in this paper is the result of a careful systematic approach toward developing a process from the test tube to the process design on a pre-pilot scale. The research was conducted in three phases as described below:

- Laboratory Scale Research for the Proof of Concept,
- Bench scale Research at Atmospheric Pressure, and
- Process Research at Pressures higher than 1 atmosphere.

Laboratory Scale Research for the Proof of Concept

Preliminary results, from the experiments conducted on the laboratory scale in microbioreactors, and published elsewhere[17], showed that in contrast to other microorganisms and microbial consortia tested, the SSII consortium showed highest growth in presence of H_2S. Moreover, SSII microbial consortium, pregrown in presence of thiosulfate showed higher removal rates of H_2S than those that were pregrown in presence of H_2S[17]. Both these data are in agreement with those observed in the literature[12,19] and support the hypothesis that microbial consortia (eg. SSII) carry out much rapid and higher reaction rates than those carried out by a culture consisting of a single bacterial species (eg. *Thiobacillus denitrificans)*[13]. The data further indicates that under anaerobic conditions, organisms growing on thiosulfate or sulfide derive their metabolic energy from the oxidation of these compounds[20], although reaction rates can be slower[19]. These preliminary data established the

technical feasibility of biological oxidation of H_2S to an outlet concentration of ≤ 4 ppm from an inlet concentration of 5, to 10,000 ppm. The experiments conducted in the microbioreactors and in the 1-L BioFlow reactor on the bench scale also indicated that the SSII microbial consortium can remove the H_2S in the SNG, and additionally remove other components of SNG, namely: COS and mercaptans (Figure 3, Table 3). Further experimental work showed that the methane is not consumed, but CO_2 is used by the SSII consortium (Figure 4). Next the removal of H_2S was tested at higher flow rates and in continuos operation for at least 96 hours (data not presented). These data indicate that the SSII consortium has the potential to adapt to the conditions that prevail in the SNG industry and the process can be scaled-up[17].

Bench Scale Research At Atmospheric Pressure

Further experiments at higher flow rates of the SSNG in the 14-L reactor established that the H_2S removal rates obtained by the SSII consortium are almost 4 times as high as those obtained by the scavenging technologies (Figure 5). At atmospheric pressure, and up to a flow rate of about $3L \bullet h^{-1}$, the H_2S removal by the SSII microbial consortium was ~ 0.4 $lb \bullet ft^3 h^{-1}$.

Experiments conducted in the 14-L bioreactor also established the following bench scale process parameters for the biological removal of the sulfur contaminants from the SSNG:

- a source of organic nitrogen is required for the microbial metabolism,
- thiosulfate is required only to initiate the removal of the target sulfur species form the SSNG,
- other contaminants, such as COS, dimethyl, ethyl and methyl mercaptans are also removed from the SSNG,
- methane is not consumed, but CO_2 is reduced (Figure 4),
- microbial activity takes place in the temperature range of 86°F to 104°F (30°C to 37°C) and pH range of 7.5 to 8.0 (Figure 6),
- two orders of magnitude (300 min to 3 min) reduction in the contact time (Figure 7) was achieved at ~ 10 fold higher SSNG flow rates ($1.2\ L \bullet hr^{-1}$ to $10.8\ L \bullet hr^{-1}$),
- the microbial process takes place at 1,000 psi but the removal rates are in the range of 0.05 $lb/ft^3 \bullet hr^{-1}$.

These data established that the SS II microbial consortium mediated process (BIODESULF™) will not only be applicable to desulfurize the sour gas stream from a variety of sources (eg. landfill gas, biogas, geothermal and other gases at atmospheric pressure); but also is potentially applicable to the SNG clean-up to pipe line quality gas resulting in the successful development of BIODESULF™ Process.

Process Research at Pressures Higher than 1 Atmosphere

Review of the data obtained from laboratory scale and bench scale research showed that for the successful application of the BIODESULF™ Process to SNG sweetening under the conditions prevalent in the SNG Processing Industry requires following parameters should be examined:

i. reduction in nutrient cost,
ii. biomass concentration effects,
iii. temperature / pH relationships at high pressure of 1,000 psi,

iv. determine minimum max for the CO_2 concentration,
v. viscosity of the processing liquid as a function of biomass loading, and
vi. if carbon steel, rather than stainless steel can be potentially used as a material for bioreactor construction.

Therefore, the subsequent experimental work was focused to investigate each of the process parameters of interest to take the biodesulfurization of SNG to the next stage of pre-pilot development and to systematically address and define each of the issues mentioned earlier.

i. **Reduction In Nutrient Cost** A number of economical sources of organic nitrogen were examined. Among those examined were the commercial sources of nitrogen such as:

- Sheftone line of products from the Sheffield Co, and
- a proprietary material called 200/20.

In addition, commercially unavailable sources listed below were also evaluated:

- a number of chicken manure from at least two different sources and at 4 different stages of the maturity of the chicken manure,
- Hoffman's dried blood available from local lawn and garden supply stores, and
- alkali digested anaerobic and activated sludge.

Analysis of the results indicated that except for the Hoffman's dried blood, all other sources were economical, nevertheless, it was difficult to obtain consistent product and hence the consistent results as explained with sterilized and unsterilized chicken manure (Figure 8). These experiments also showed that the commercially available organic sources of nitrogen establish consistent and repeatable process parameters (Figure 8). Among these, the product called 200/20 not only is most economical, but also gave the highest H_2S removal rate of 0.11 lb/ft^3h^{-1} (Figure 9).

ii. **Biomass Concentration Effects** Preliminary data from the microbioreactors and the data at the atmospheric pressure (inset Figure 10) indicated that with an increase in the biomass loading from 0.5% to 1.0 % (wet weight of cells to volume of the liquid in the reactor), the rate of biodesulfurization of H_2S from the SSNG increased from about 0.05 to 0.146 lb/ft^3hr^{-1} (Figure 10, inset). With this background, once the SSII consortium started giving the desirable removal rates at 1,000 psi, the effect of biomass loading at high pressure was also evaluated. Since the results from experiments at atmospheric pressure, already established the base line of 1% (wt/v) microbial loading, at 1,000 psi effect of 10% biomass loading was evaluated. The data show that SSII microbial consortium adapted to both, a pressure of 1,000 psi and a temperature of 140°F (60°C) could remove the H_2S at a rate of 1.0 lb/ft^3hr^{-1} (Figure 10). This rate is 10 fold higher than that obtained by the Scavenger Technologies[4,9,15-17]. According to M.W. Kellogg analysis[15], at this rate of H_2S removal and considering that the sulfur procesing cost downstream of the bioreactor remain the same as for Liquid Redox Technologies, the liquid required for treating 1 TPD sulfur by the SSII microbial consortium mediated BIODESULF™ Process is only 600 gallons, in contrast to 4,000 gallons for the ARI-LO-CATII™ and 10,000 gallons for the BIO-SR™ Technology. These data indicate that with BIODESULF™, mediated SNG treatment, the cost for 1TPD sulfur treatment would be 6.7 and 16.7 fold less than that for Liquid

Redox and BIO-SR™ respectively. Thus, the cost-effectiveness of the BIODESULF™ Process is self evident.

iii. **Temperature / pH Relationships At High Pressure Of 1,000 Psi** The next important parameter to be established was the effectiveness of SSII microbial consortium to remove H_2S at temperatures and the pHs that are commonly encountered in the SNG streams. From the data obtained on these experiments conducted at atmospheric pressure, the pH range was established to be between 7.5 to 8 Figure 6) and the temperature range to be 86°F to 104°F (30°C to 40°C). However, the actual pH of the reaction mixture when the H_2S was passed through the system was still not established, nor was the range at 1,000 psi. Also, the effective temperature range for the process was still not established. Based on the input from GRI, it was also certain that the process temperature range has to be higher than that obtained during the batch experiments (Figure 6). Therefore, a series of experiments were conducted where the inoculum was grown at room temperature (77°F, 25°C) and the H_2S removal was evaluated at temperatures of 50°F, 104° F, 120° F, 140°F and 158°F (10°C, 40°C, 50°C, 60°C and 70°C) and 1,000 atm pressure in the Parr pressure reactor. The data (not presented) established the range of temperature in which the SSII microbial consortium could remove the H_2S. However,, as one would expect, the rates were different in each case and in some cases were not even compatible with the needs of the SNG Processing industry.

Therefore, a program was started to adapt the SSII microbial consortium to carry out the sweetening of SNG at rates desired by the SNG Processing industry. As a result, the SS II consortium could now remove the H_2S in the desired temperature range. The important observation was that with the increase in the process temperature range, the rate of H_2S to sulfur conversion also increased linearly (Figure 11). These data confirm:

- the hypothesis that increase in temperature can enhance the stability of a biological process to a certain extent, and

- the metabolic mechanism of bioconversion of H_2S to sulfur, or sulfur species is mediated by thermostable enzymes, because these enzymes are much more stable than their mesophilic counterparts and with an increase in the incubation temperature, the rates of reaction can be enhanced up to an order of magnitude[14,18].

Iv **Range Of CO_2 Concentration** One of the recommendations of the M.W. Kellogg report[15], was also to evaluate the range in which the CO_2 present in SSNG is removed by the SSII microbial consortium. Therefore, the experiments conducted to evaluate the removal rates of H_2S were repeated. This time, however, in addition to evaluating only the H_2S removal, at the same time points as those taken for the H_2S, additional headspace samples from the Parr reactor were analyzed on a GOW-MAC Gas chromatograph equipped with TCD. The data (Figure 11) clearly indicate that at higher temperatures (up to 140°F, 60°C), not only is the sulfur removal enhanced, but also the CO_2 removal is increased. These data have an important bearing on the overall process economics. In one step, one can remove a number of contaminants (H_2S, CS_2, dimethyl, ethyl and methyl mercaptans and CO_2) from the SSNG and thus enhance the calorific value of the processed SNG, which is now sweetened. These data further support the hypothesis that under anaerobic conditions, the chemoautotrophic bacteria utilize CO_2 as the source of carbon[2,5,19]. Thus, the possible mechanism of bioconversion of reduced sulfur species (eg. H_2S) to elemental sulfur by the SSII microbial consortium might involve the

utilization of H_2S as a source of energy and CO_2 as a source of carbon, when either NH_4^{+1}, or NO_3^{-1} or both are present in the culture medium as is the case for the BIODESULF™ Process.

v **Viscosity of The Process Liquid as a Function of Biomass Loading** The viscosity of the culture media and the culture broth can have a strong detrimental effect on the operating costs of the process, especially at biomass loadings of ≥ 10% (wet weight to volume). This can lead into higher capital costs for the pumps, filtration and other PID equipments as well as higher operating costs in electric power. Therefore, a series of experiments were run to determine the viscosity of the culture broth with the loadings of SSII microbial consortium in the range of 0% to 15% (wet cell weight to liquid volume). The data were collected using a viscometer calibrated with distilled water and microbe-free sterile CSTDM. Both, the density as well as the kinemetic viscosity were very near that of the water (Table 4). Therefore the viscosity of the culture broth should not pose any detrimental hurdles in the operation of the process. Also the economics of the process should not be affected.

Vi **Carbon Steel as a Bioreactor Material** Even though stainless steel (SS 316) has always been used as the material of construction for the reactors to process SNG, especially because of H_2S contamination, an investigation of the corrosion studies was undertaken to further reduce the capital cost. The rate of corrosion was estimated with coupons of carbon steel and stainless steel of the total dimension of 9.54 inch^2 (LxW). These coupons were immersed in culture medium inoculated with the SSII microbial consortium. The controls were the medium alone and the biotic control was prepared in the manner described in Table 2. The coupons (three coupons of a kind to each bioreactor) were incubated in each of the treatments for a period of 14 days. After 14 days, the coupons were washed with water, distilled water and 70% ethanol and finally air dried. The coupons were examined under the dissecting microscope to observe for pitting and other physical signs of corrosion. Subsequently, the coupons were weighed in an analytical balance to note the changes in the weight before and after the treatment period. From these data the corrosion rate in mils per year (mpy) was calculated from the formula:

$$CR = (W \bullet 534) \div (A \bullet t \bullet D)$$

where,

CR	=	Corrosion rate,
W	=	Weight loss = W_i - W_f,
W_i	=	initial weight of the coupon of the test material,
W_f	=	final weight of the coupon of the test material
534	=	proportionality constant
A	=	Area of the coupon of the test material
t	=	experimental time in hours
D	=	density of the test material

The data (Table 5) shows and reconfirms that the SS 316 was much less corroded than the carbon steel, whereas carbon steel actually favored the growth of the SS II microbial consortium (Table 5). As is noted by a net increase in the OD_{460} of the culture broth before and after conducting the corrosion experiments.

Vii Economic Analysis M.W. Kellogg personnel have been performing the economic analyses of a number of processes for GRI[14,16]. The assumptions that they used to make these calculations, have recently been reviewed and used by Rehmat et al.[16] to calculate the economics for the BIO-SR™ Process. Using the same assumptions, and the data obtained from different experiments in the study reported here, the preliminary economics for the BIODESULF™ process was calculated based, also on the analysis of the BIODESULF™ process by M.W. Kellogg[15]. On this basis, the BIODESULF™ process is least costly (figure 12) of all the processes being used or developed for processing the SNG at least up to the production level of 2 MMSCFD.

CONCLUSIONS

In summary, the results reported herein show that BIODESULF™ process removes the hydrogen sulfide at 1 $lb/ft^3\ hr^{-1}$. This rate of removal is 10 fold higher than that obtained by the scavenger technologies. The data also indicate that this is potentially the most cost-effective process in contrast to the state-of-the art technologies, at least up to the production level of 2 MMSCFD. Furthermore, up to 140°F, a direct relationship exists between temperature and H_2S removal rates and those of CO_2 removal. Some of the other salient features of the BIODESULF™ Process are as follows:

- not only is the nutrient cost significantly reduced with 200/20, the removal rates are also enhanced,
- the rate of removal is further enhanced with an increase in the biomass concentration,
- increase in biomass does not significantly affect the viscosity or density of the processing liquid, and
- SS 316 is the most suitable reactor building material.

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REFERENCES

1. Bryant, M.P. 1972. Am. J. Clin. Nutr., **25:** 1324.

2. Cadenhead, P. and Sublette, K. 1990. Oxidation of Hydrogen Sulfide by Thiobacilli. Biotechnol. Bioeng., **35:** 1150-1154.

3. Dalrymple, D.A., Trofe, T.W., and Evans, J.M. 1989. An Overview of Liquid Redox Recovery. Chemical Engineering Progress, May 1989, pp 43-49.

4. Dalrymple, D.A and Wessels, J.K. 1996. Research Summary. Proc.1995 GRI Liquid Redox Sulfur Recovery Conference, Austin, Tx, pp. v-x.

5. Gadre, R. 1989. Removal of Hydrogen Sulfide from Biogas by Chemoautotrophic Fixed-Fil Bioreactor. Biotechnol. Bioeng., **34:** 410-414.

6. Hobbie, J.E., Daley, R.J., and Jasper, S. 1977. The Use Of Nucleopore Filters For Counting Bacteria By Fluorescence Microscopy. Appl. Microbiol., **33:** 125-1228.

7. Hungate, R. 1969. In, "Methods in Microbiology", **3B**, Norris, J.R. and Ribbons, D.W. (Eds.), Academic Press.

8. Leppin, D., Evans, J.M., and Krist, K. 1991. Gas Research Institute Program in Sulfur Recovery Research. Proc. GRI Liquid Redox Sulfur Recovery Conference, Austin, Tx, pp. 387-411.

9. Leppin, D.1996. Overview of Liquid Redox Sulfur Recovery and H_2S Scavenging Processes. Proc. 1995 GRI Liquid Redox Sulfur Recovery Conference, Austin, Tx, pp. 3-10.

10. Leppin, D.1996. Overview of GRI's Sulfur Recovery Research Program. Proc.1995 GRI Liquid Redox Sulfur Recovery Conference, Austin, Tx, pp. 11-16

11. McCarthy, A.J. 1987. Lignocellulose-degrading Actinomycetes. FEMS Microbiol. Rev., 46:145.

12. McManus, D. 1996. The Development, Chemistry and Applications of Chelated Iron Sulfur Recovery Processes. The 3rd International Petroleum Environmental Conference, Albuquerque, NM, USA September 24-27,1996.

13. Plas, C. Harant, H., Danner, H., Jelinek, E., Wimmer, K., Holubar, P., and Braun, R. 1992. Ratio of Biological and Chemical Oxidation During the Aerobic Elimination of Sulfide by Colorless Sulfur Bacteria. All Microbiol., Biotechnol., **36:** 817-822.

14. Quinlan, M.P., and Echterhoff, L.W. 1993. Technical and Economic Comparison of LO-CAT II™ with other iron-based Liquid Redox Processes. Proc. 1992 GRI Liquid Redox and Sulfur Recovery Conference, Austin, Tx., pp 179-220.

15. Quinlan, M.P., Guillroy, G., and Floyd, F.M. 1995. Evaluation of ARCTECH's Biological Process for H_2S Removal. Gas Research Institute Report for the Contract # 5088-221-753, 18 pages.

16. Rehmat, A. and Goyal, A. 1995. BIO-SR™ Technology Update. Proc. 1995 GRI Liquid Redox Sulfur Recovery Conference Proc., Austin, Tx, pp. 41-55.

17. Srivastava, K.C. 1993. Biological Removal of H_2S from Sour Natural Gas. Proc. 1992 GRI Liquid Redox and Sulfur Recovery Conference, Austin, Tx. pp 131-146.

18. Srivastava, K.C. 1989. Saccharification of Lignocellulosic Biomass by Actinomycetes: A Comparative Study with Meso- and Thermophiles. TAPPI Proc. Internat'l. Symp. Wood Pulping Chem., 2: 227-232.

19. Sublette, K.L. and Sylvester, N.D. 1986. Microbial Desulfurization of Gases. Biotechnol. Bioeng. Symp., 17: 543-564.

20. Suzuki, I and Werkman, C.H. 1959. Proc. Natl. Acad. Sci., **45**:239.

21 Walia, D.S., Srivastava, K.C. and Barik, S. 1992. Proc. 12th Annual Gasification & Gas Stream Clean-Up System Contractors Review Meeting, **1**: 535, METC, Morgantown, WV.

Table 1: Composition Of The Standard Mix For The Analysis Of Sulfur Species In The Culture Broth Of SSII Consortium

	Quantity (in mL) to be added for the following sulfur species			
Standard Mix	S^{-2}	$S_2O_3^{-2}$	SO_3^{-2}	SO_4^{-2}
Standard 1	0.5	2.0	1.5	0.5
Standard 2	1.0	4.0	3.0	0.1
Standard 3	1.5	6.0	4.5	1.5
Standard 4	2.0	8.0	6.0	2.0

Table 2: Experimental Design For The Preliminary Screening To Determine The Most Efficient Microorganism For The Oxidation Of Hydrogen Sulfide

Treatment	No Microorganisms	SSI	SSII	AMD1	TD	TF
	Abiotic Control		√			
Killed biotic Control		√	√	√	√	√
Biotic		√	√	√	√	√

Figure 1: Experimental Set-up for the 2L and 14L Reactors

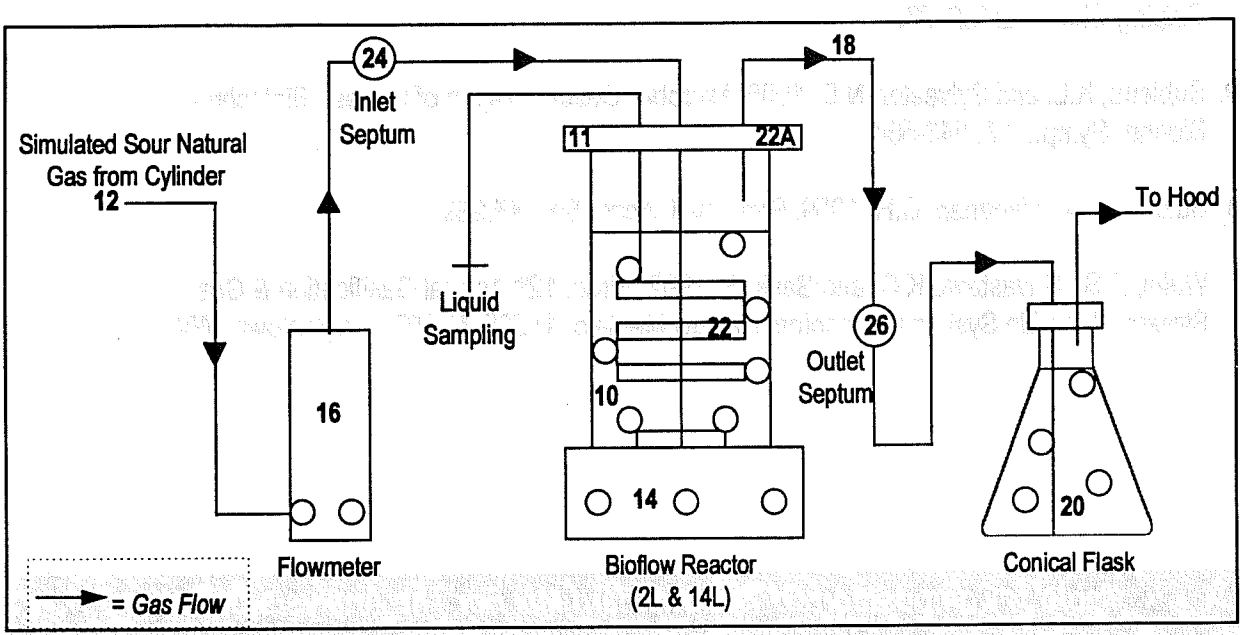


Figure 2: Experimental Set-up for the 2L and 14L Reactors

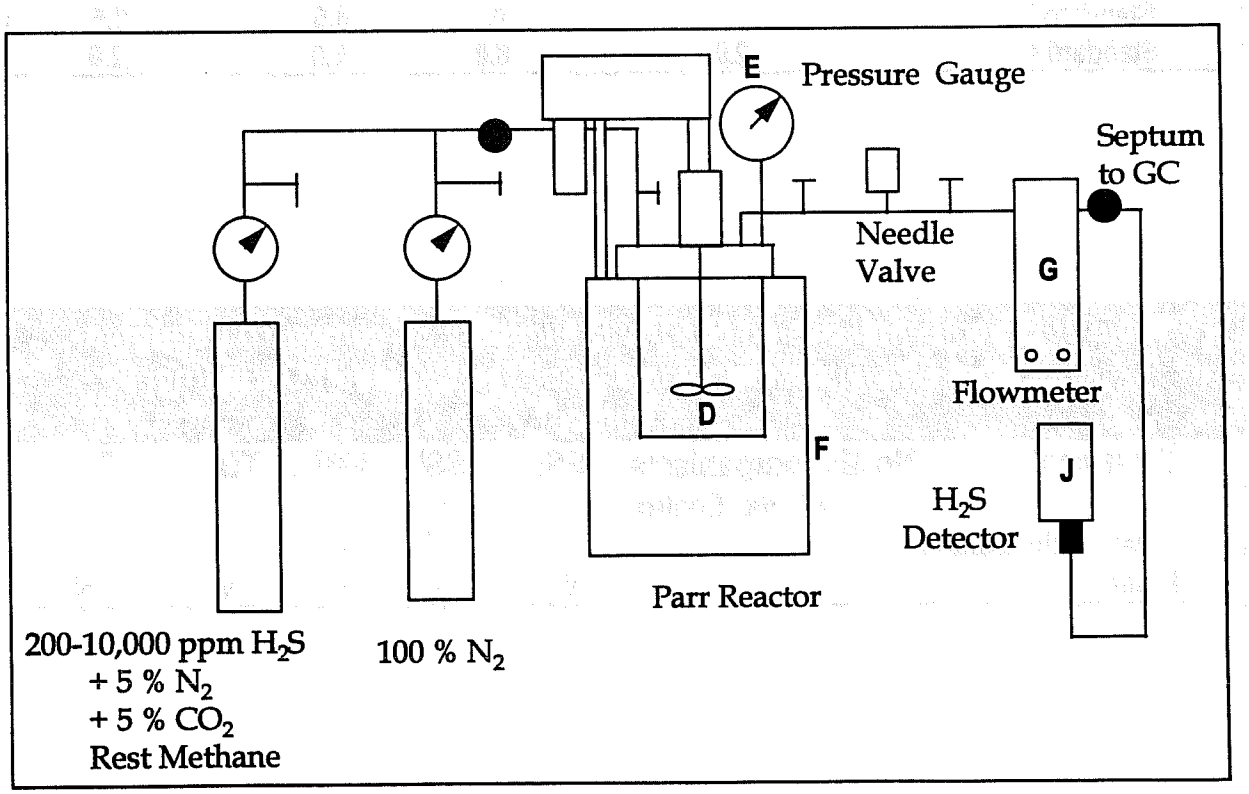
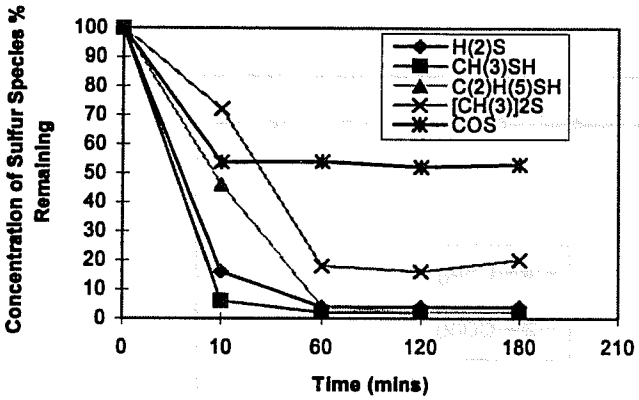


Figure 3: Other Sulfur Contaminants Common to the Sour Natural Gas are also Mitigated in BIODESULF™ Process



Inlet Concentrations (in ppm) are as follows:
5,000 for H_2S, 1000 for each of CH_3SH, C_2H_5SH and $(CH_3)_2S$, 1,500 for COS

Table 3: Removal Rates of Sulfur Species Present in Simulated Sour Natural Gas by the SS II Microbial Consortium Mediated BIODESULF™ Process

Sulfur Species	Removal Rates (lb/ft^3-h)
Hydrogen sulfide (H_2S)	0.300
Mercaptans	
dimethyl ($[CH_3]_2S$)	0.030
ethyl (C_2H_5SH)	0.021
methyl (CH_3SH)	0.021

Figure 4: BIODESULF™ Process Does not Consume Methane (CH_4), but Mitigates carbondioxide (CO_2)

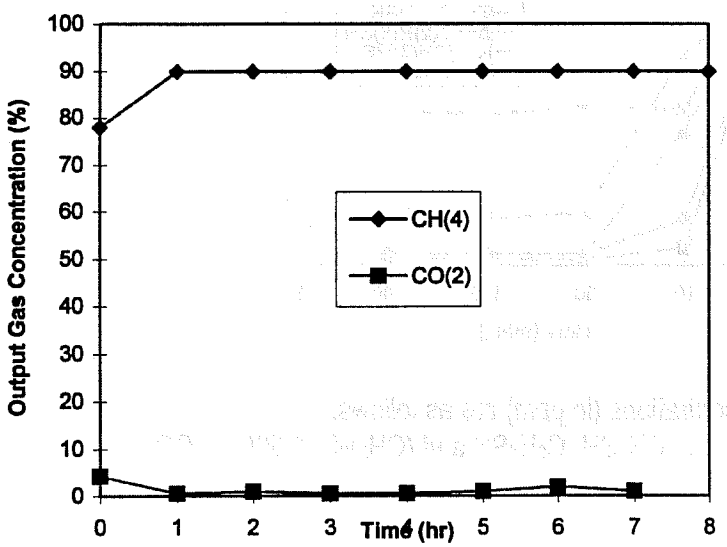


Figure 5: Initial H_2S Removal Rates are Comparable to Those From Scavenging Technologies

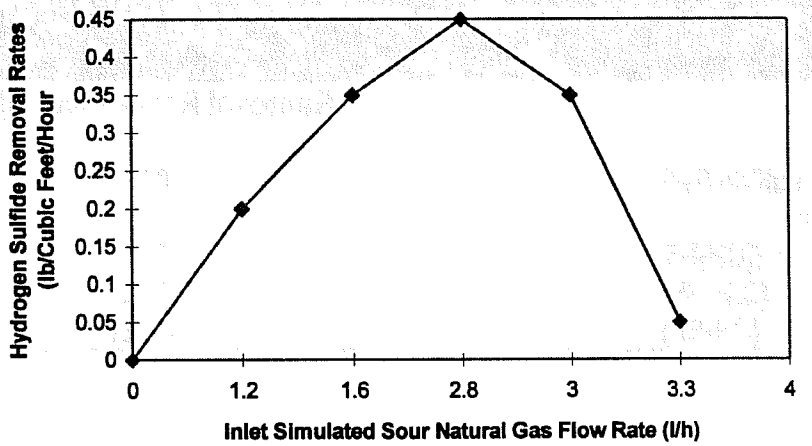


Figure 6a: Preliminary Studies Showed Highest H_2S Removal at pH of 7.5 to 8

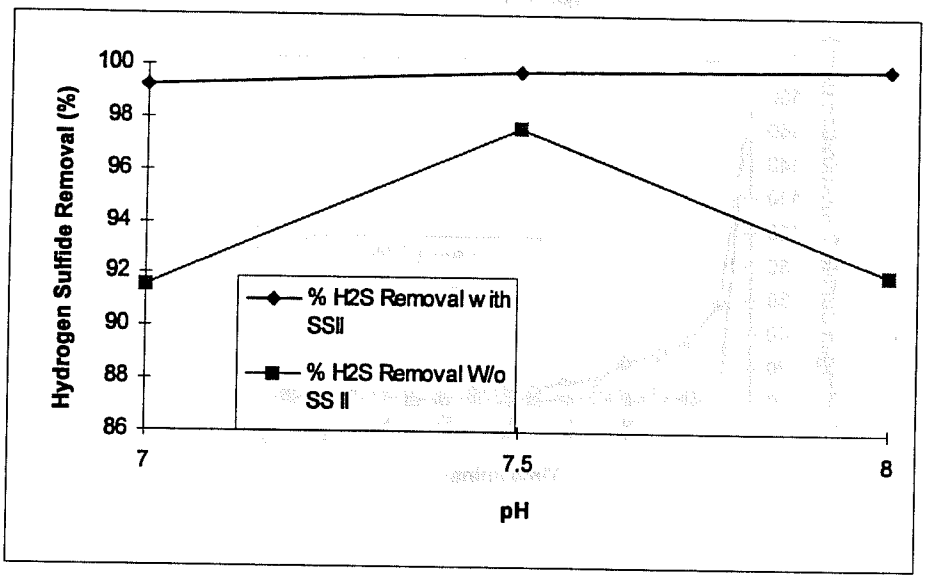


Figure 6b: Preliminary Studies Showed Highest H_2S Removal at 30°C

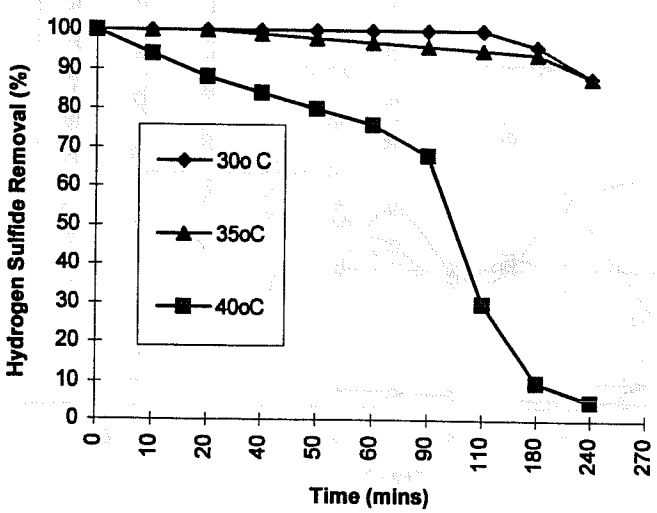


Figure 7: Contact Time Reduced By Two Orders of Magnitude (300 to 3 mins) at Ten Fold Higher Flow Rates

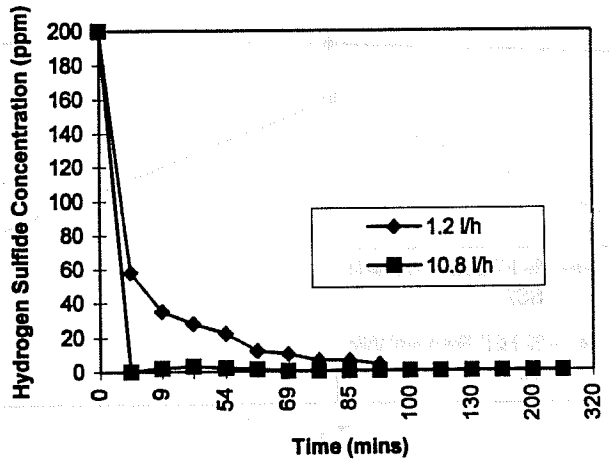


Figure 8: In Contrast to chicken Manure, Commercially Available Organic Sources of Nitrogen Provide Consistent Results

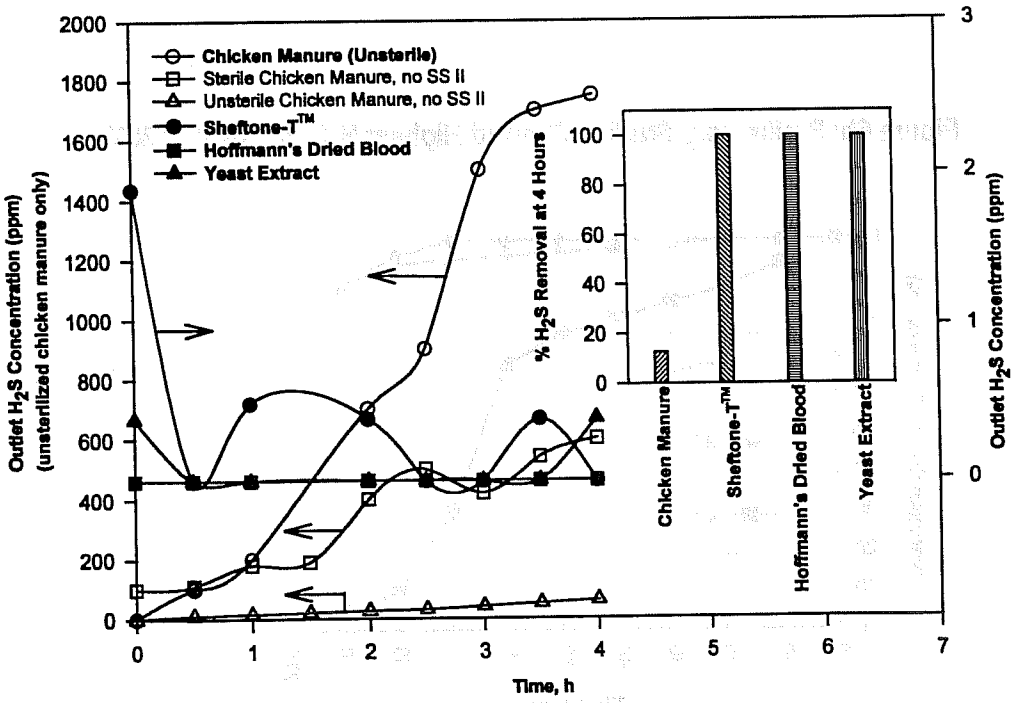
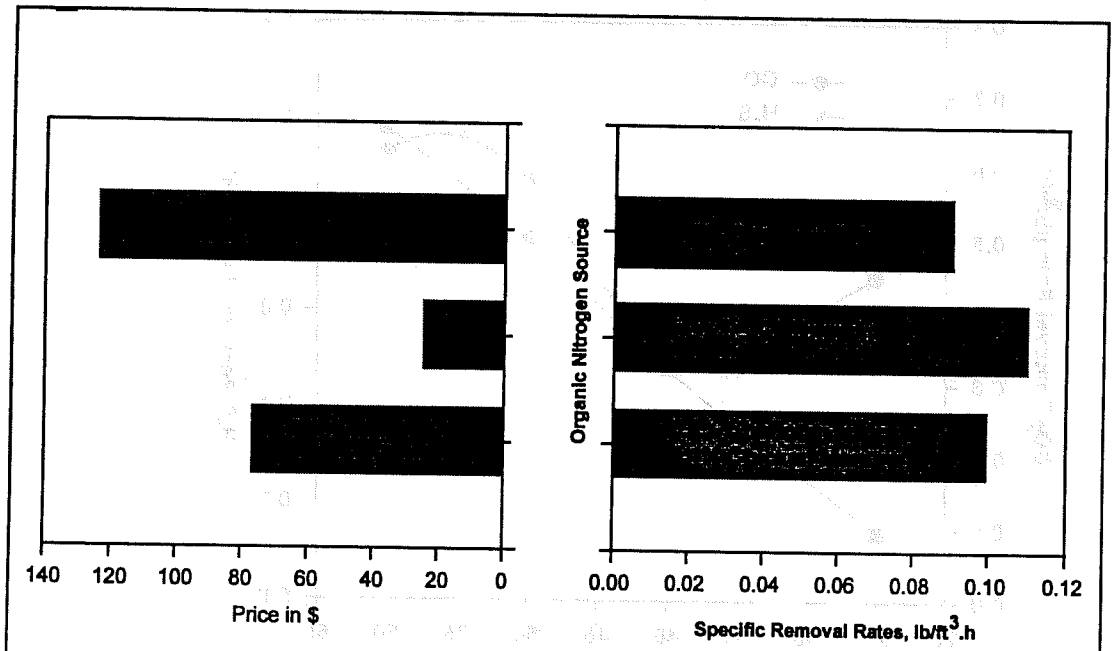
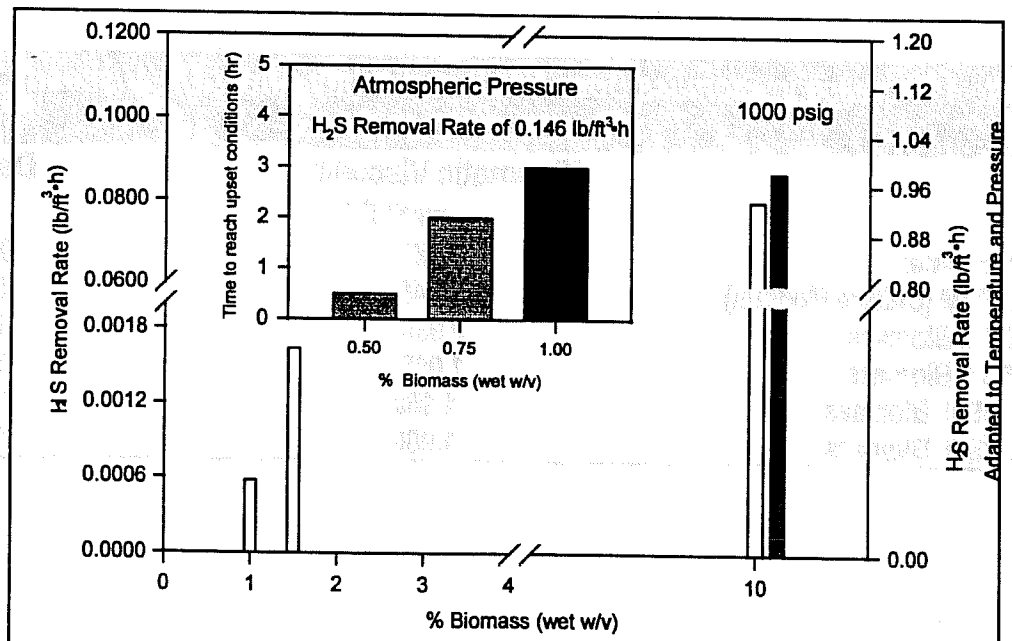


Figure 9: The Cost of Nutrient Medium is Significantly Reduced with Product 200/20 Without Compromising H_2S Removal Rates



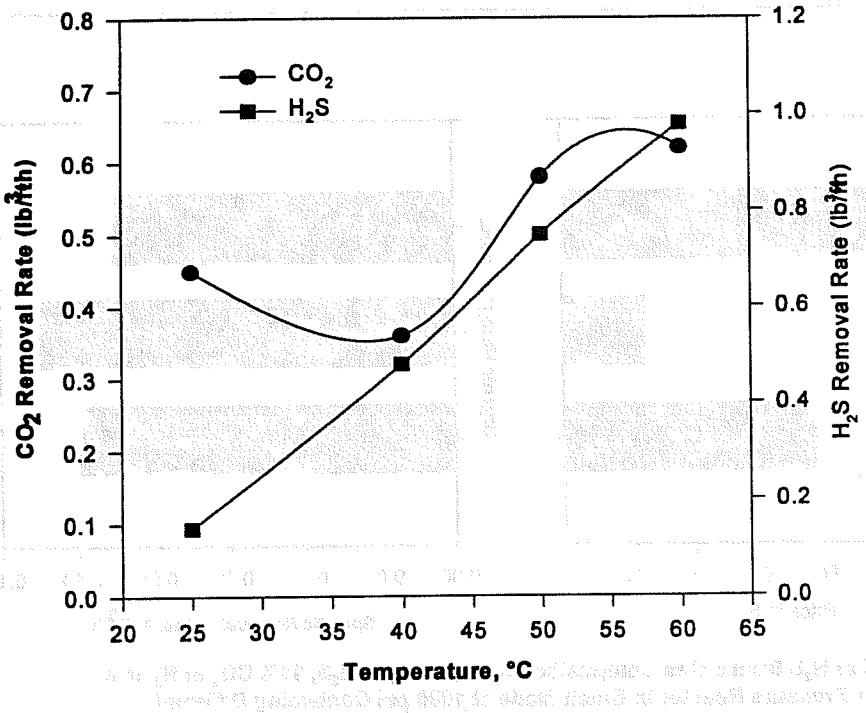
Removal of H_2S from a Gas Composition of 10,000 ppm H_2S, 10% CO_2 in N_2, in a Parr Pressure Reactor in Batch Mode at 1000 psi Containing Different Sources of Organic Nitrogen with 10% (Wet w/v) SS II

Figure 10: At 1000 PSI and Up to 140°F (60°C) the H_2S Removal Rates are Directly Related to an Increase in Biomass



Increase in Biomass Loading of up to 10% Enhances the H_2S Removal Rates Independent of the Pressure

Figure 11: At a Higher Temperature, Both CO_2 and H_2S Removal is Enhanced



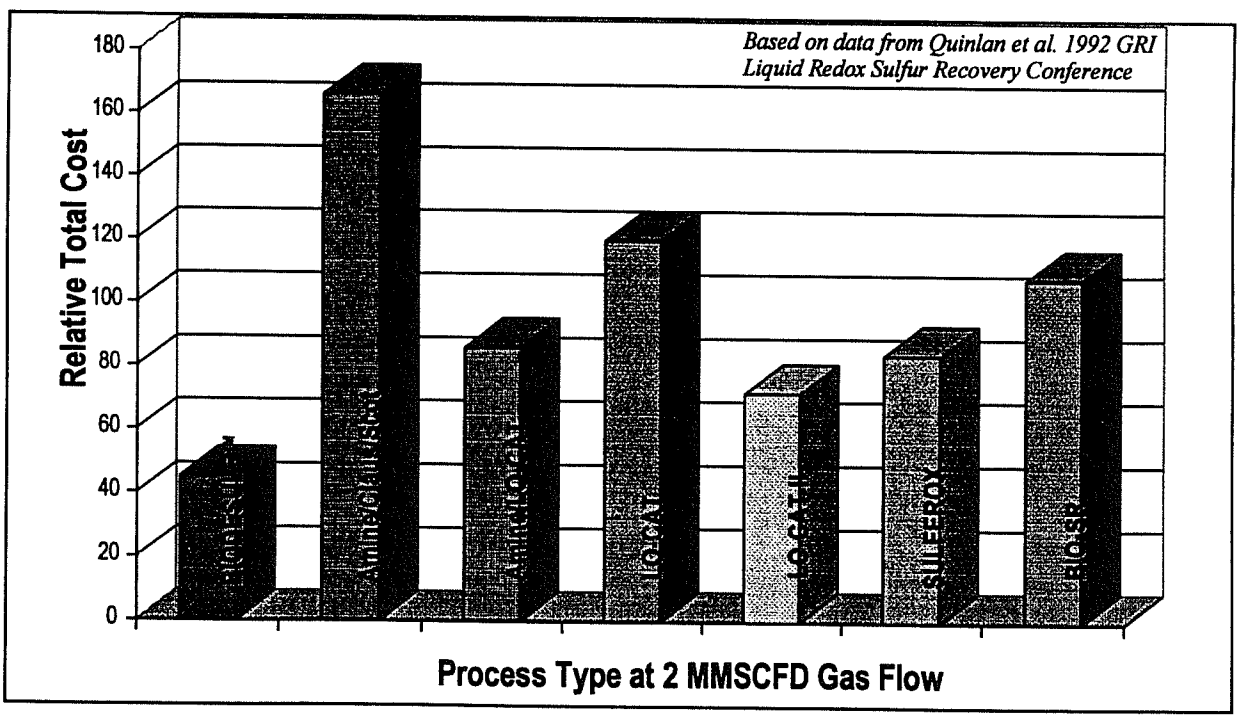
The Rate of Removal of CO_2 and H_2S at different temperatures in 1-L Parr Pressure Reactor with 10 % SS II + 0.2 % Cargill 200/20 at 1000 psi

Table 4: Increase in Biomass Does Not Significantly Affect The Viscosity Or Density of Liquid

Fluid	Kinematic Viscosity $mm^2 S^{-1}$	Density
Distilled Water	0.885	0.9997
5 X CSTDM (Culture Medium)	0.945	1.0240
1.0% SS II Biomass	0.930	1.0240
5.0% SS II Biomass	1.005	1.0260
10.0% SS II Biomass	1.180	1.0270
15.0% SS II Biomass	1.980	1.0400

Table 5: Stainless Steel 316 Is A Better Bioreactor Construction Material As Shown By The Corrosion Studies		
Parameters Evaluated	**Bioreactor Construction Material Evaluated**	
	Carbon Steel	**Stainless Steel 316**
	Loss in the Weight (in Grams)of	
Coupon Over 14 day test period	**0.030**	**0.007**
Change in the pH of the liquid	**0.410**	**0.390**
Biomass growth as OD460	**0.880**	**0.420**
Corrosion rate in mils per year (mpy)	**0.500**	**0.130**

Figure 12: The BIODESULF™ Process is Cost-Effective



Mechanisms of Anthraquinone Inhibition of Sulfate-Reducing Bacteria

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L. B. Gosser, E. I. DuPont de Nemours

ABSTRACT

This paper presents evidence that anthraquinone derivatives have potential for use in mitigating sulfide production from sulfate-reducing bacteria (SRB). It is proposed that these chemicals could be uniquely useful in oilfield and industrial applications where cost effectiveness and human and environmental safety are paramount.

It has been shown that anthraquinones inhibit sulfate respiration, but not aerobic respirations, rendering it safe for use in many wastewater treatment applications. We propose that this specificity is due to the ability of anthraquinones to equilibrate electron flow in the membranes of *Desulfovibrio*. In this report we demonstrate a positive correlation between inhibition of sulfate respiration by anthraquinones and their reactivity with cytochrome c_3, which is a protein considered to be diagnostic of SRB. A consequence of this equilibration is that ATP synthesis is uncoupled from respiration. Since sulfate activation has a unique requirement for ATP, the process of sulfate reduction halts with the depletion of ATP level. A model for inhibition of SRB whereby anthraquinone "short circuits" electron transfer, resulting in a loss of ATP synthesis, is discussed. This is consistent with the specific inhibition of sulfate respiration in contrast to other respiration processes which do not require ATP.

Inhibition of SRB within a biofilm is dependent upon the form of the anthraquinone and system hydraulics. A model is proposed to explain differences in efficacy within the biofilm between soluble and insoluble forms of anthraquinone. Anthraquinone particle size is a key parameter affecting SRB inhibition. Oilfield applications are discussed. Since anthraquinone is a non-toxic compound, its use provides an environmentally acceptable alternative to biocides for the control of SRB in oilfield systems.

INTRODUCTION

Sulfate-reducing bacteria (SRB) typically are abundant in oilfield waters, both in seawater used for waterfloods and in waters produced with crude oil. Uncontrolled growth and activity of SRB can create severe operational, environmental, and human safety problems, including corrosion, solids production, and hydrogen sulfide (H_2S) generation. Environmental conditions found in oilfield reservoirs and surface systems are especially conducive for microbial growth due to the presence of volatile fatty acids and sulfate.

Studies have shown that a group of structurally-related derivatives of 9,10-anthraquinone effectively inhibit the process of sulfate respiration in SRB at μmolar concentrations without having a bactericidal effect on the bacteria (1, 2). Anthraquinone is generally non-toxic to plants and animals and is relatively unreactive in the presence of the typical constituents in a biofilm. It therefore can transport quite easily into the biofilm on a pipe or vessel wall, contacting the SRB without reduction in its concentration. The anthraquinone is chemically unaffected by other bacteria or the exopolysaccharide matrix present in the biofilm. The only factor limiting its availability for SRB is the fact that anthraquinone itself is essentially insoluble in water and therefore it must physically penetrate the biofilm voids by dispersion and other transport processes. This limitation has been minimized by the use of a soluble ionic form of anthraquinone in treating most anaerobic oilfield systems.

Since typical biocide treatments in the oilfield are not able to sterilize the systems, regrowth of the bacteria occurs quite rapidly within the biofilm. Biocides therefore can only be used to control the growth and activity of the bacteria even though their function is to be cidal. On the other hand, anthraquinone treatments are specifically designed as a biostatic control of SRB activity. Inhibition of SRB activity will typically extend for a longer duration than the regrowth period following a biocide treatment, thereby more effectively controlling sulfide production than with a biocide itself.

This paper presents evidence to support a mechanistic model for the inhibition of the SRB whereby anthraquinone uncouples electron transfer from ATP synthesis. It is proposed that this is due to the redox-active nature of the anthraquinone. Also presented will be a model which describes the application of anthraquinone treatments to inhibit sulfide production within a fully-developed biofilm.

MATERIALS AND METHODS

Desulfovibrio gigas was used as the model test strain in all experiments performed with pure cultures of sulfate-reducing bacteria or with membrane

preparations from sulfate-reducing bacteria. Crude enrichment studies were performed with environmental samples inoculated into a lactate-sulfate based growth medium designated BTZ-3 (3). Determination of growth and sulfide formation with these samples were performed as previously described (3).

The time course study to compare the effects of anthraquinone form and dose regime was performed using a mixed population of bacteria obtained from coupons within the Prudhoe Bay, Alaska, seawater injection system. The bacteria were inoculated into modified lactate-sulfate Postgate's B medium, treated with either a water dispersion of 9,10-anthraquinone particles (90% less than 2.0 μm) or a mixture of two water-soluble disodium salts of anthraquinone (9,10-dihydro-9,10-dihydroxyanthracene and 9,10-dihydroxyanthracene), and incubated at 30°C. Treatments were made at 10 or 50 ppm of equivalent anthraquinone once or on four successive days. Periodically the liquids were sampled for total sulfide by the method of Siegal (4) with the color due to methylene blue formation read at 670 nm.

Spectrophotometric determination of the oxidation of cytochrome c_3 was performed using cytochrome c_3 purified from *D. gigas*. The cytochrome was purified as described by LeGall et al. (5) Experiments were performed in serum-stoppered quartz cuvettes under an argon atmosphere. The cytochrome was titrated to its maximum reduction, as evidenced by the 552 nm absorption peak, by incremental additions of sodium borohydride. After determining that the reduced cytochrome was stable, anaerobic acetone solutions of either 2-chloro-3-carboxyanthraquinone or anthraquinone-1-sulfonic acid were added incrementally by syringe. The rate of reoxidation of the reduced cytochrome was then determined by monitoring the rate of change in the 552 nm absorption peak.

For experiments involving sulfide generation from a biofilm the following method was used. Biofilm was generated on aquarium rocks by incubating the rocks in wastewater obtained from a local wastewater treatment plant. The wastewater was supplemented with 10 mM sodium sulfate and allowed to stand over the rocks for several weeks with weekly replenishment of the wastewater. After establishment of the sulfide-producing biofilm, the rocks were placed within the cylinder of a 25 ml disposable syringe. To achieve fixed but varying flow rates, different syringes were set up using different gauge needles to achieve the desired flow rate of wastewater through the syringe. The experiment was performed by passing a 10 ml volume of water containing either 500 ppm of anthraquinone particles (90% less than 2.0 μm) or 28 ppm of water-soluble 1,4-dihydro-9,10-dihydroxyanthracene, disodium salt, through the syringe. The anthraquinone was then washed out of the rock-filled syringe with 10 volumes of wastewater at the same flow rate. The syringes were then capped and allowed to incubate overnight before sulfide was measured in the headspace of the syringe.

RESULTS AND DISCUSSION

Previous work has shown that 9,10-anthracenedione (9,10-anthraquinone) and many simple derivatives of this compound are effective inhibitors of SRB and, under certain conditions, methanogenesis (3). 1,8-Dihydroxyanthraquinone has been shown to inhibit both growth and sulfide generation from sulfate-reducing bacteria of the genus *Desulfovibrio* (3). This inhibition was shown to be associated with the uncoupling of ATP synthesis during electron transfer from hydrogen to fumarate using French Press derived membrane particles. Due to its superior aqueous solubility, and ease of spectroscopic quantitation, the 1,8-dihydroxyanthraquinone was also used in these laboratory studies on the mechanism of action. Studies directed toward understanding efficacy in the field, or in treating biofilms, utilized the commercial Sulf Control® formulation comprised of the more insoluble 9,10-anthraquinone as a 50% dispersion in water. The two compounds have similar overall activity and it is assumed that the proposed mechanism is applicable to either compound.

The present report extends our understanding of the mechanism and specificity of inhibition by implicating cytochrome c_3 as a "reactive site" with anthraquinone. Data are also shown that suggest the physical form of the anthraquinone is critical to its effectiveness.

Evidence for Sulfide Suppression

Figure 1 shows that the sulfide generation rates vary substantially between samples from different sites and that the 1,8-dihydroxyanthraquinone generally suppresses sulfide generation in environmental samples derived from three distinct anaerobic habitats. All samples were enriched for sulfate-reducing bacteria by employing the same lactate-sulfate based enrichment medium. It can be reasonably expected that different species of *Desulfovibrio* will be present in freshwater, saltwater and anaerobic digestor habitats and the possibility that the identical species were enriched in every case is unlikely. The data show significant suppression of sulfide in all samples except the three noted as WD from the Wilmington, Delaware, anaerobic digestor facility. The WD samples apparently contain a resistant species of *Desulfovibrio*. The resistant organism was isolated and appears to be a typical species of the genus *Desulfovibrio* based on morphology, pigment content and nutrition (data not shown).

A representative time course of sulfide production for a mixed oilfield population in the presence and absence of two forms of anthraquinone is shown in Figure 2. We have found that anthraquinone treatments, even at extraordinarily high dose levels, usually do not result in permanent suppression of sulfide production. Typically, as shown in the figure for both forms of the anthraquinone at 10 ppm and even at 50 ppm for the soluble form, sulfide suppression ceases after a period of several days. However, multiple daily treatments were effective

at inhibiting these bacteria for at least seven weeks. Aliquots of these inhibited bacteria inoculated into fresh medium after 34 days confirmed viability, with absorbance readings after 96 hours in excess of 1.1 O.D. for all samples.

Resumption of sulfide production may be a consequence of physical partitioning of the anthraquinone out of the bacteria into non-aqueous phases, biodegradation of the anthraquinone, and/or removal of its availability to the SRB due to agglomeration of particles. The solubility of anthraquinone in water is less than 0.1 ppm. Hence, most of the chemical settles to the bottom of the serum bottle. However, this is also true of the soluble form since the disodium salts are soluble only in a high pH solution. Injection of low concentrations into the medium does not alter the medium pH significantly and therefore results in the formation of molecular anthrahydroquinones with limited solubility. This latter process forms extremely small particles of the anthrahydroquinones which appear to more effectively inhibit the SRB and possibly do not agglomerate as much as the anthraquinone. Agglomeration might account for the increase in sulfide production of the multiple anthraquinone-treated culture after nine days while the anthrahydroquinone-treated bacteria remained inhibited. The same is true for the single-treated cultures.

Mechanism of Action

Previous work has shown that 1,8-dihydroxyanthraquinone (I_{50}=1.6μM, where I_{50} is the concentration required for 50% inhibition of sulfide production) and to a lesser degree the 2-chloro-3-carboxy derivative (I_{50}=8μM) were both effective at sulfide suppression and also were shown to uncouple ATP synthesis in membrane preparations of *Desulfovibrio gigas* (3). However, the anthraquinone-1-sulfonic acid derivative was shown to be completely ineffective at both sulfide suppression and at uncoupling ATP synthesis, even at extraordinarily high concentrations. Secondly, we have shown that anthraquinone can overcome the inhibition of electron transfer induced by compounds such as 2-heptyl-8-hydroxyquinoline-N-oxide. This latter observation strongly supports the idea that the anthraquinone functions as an electron transfer agent within the cell membrane of *Desulfovibrio*. The observations taken together suggest that anthraquinones may be redox active uncouplers of ATP synthesis. However the precise points of interaction of anthraquinone with the respiratory chain of *D. gigas* have been speculative.

The respiratory chain of *Desulfovibrio* is dominated by cytochrome c_3, which is a low molecular weight electron transfer protein found on, and in, the membrane of SRB. This protein is restricted to the sulfate-reducers and functions in electron transfer to and from the hydrogenase enzyme. The protein is also known to undergo reversible oxidation-reduction reactions at very low potentials (-300 to -400 mV) which are close to those for anthraquinones (~ -500 mV) (6).

We postulated that anthraquinone may be specifically reactive with the cytochrome c_3 and this may be the basis for redox uncoupling and specificity.

Figure 3 shows the difference in chemical reactivity with cytochrome c_3 of an anthraquinone which is a sulfide suppresser (2-chloro-3-carboxy-) compared to an anthraquinone with no activity toward SRB. These particular anthraquinones were chosen for this study because they were both sufficiently soluble to enable the measurements and, secondly, one was an inhibitor and the other not. The data show the ability of pre-reduced cytochrome c_3 to be chemically reoxidized by the anthraquinone. Rates of re-oxidations were measured spectrophotometrically at 552 nm and reciprocally plotted as a function of anthraquinone concentration. Figure 3 shows that indeed the rate of reoxidation is faster with the sulfide inhibitor than with the anthraquinone-1-sulfonic acid. The concentration of the 2-chloro-3-carboxy derivative required for a discernible rate is also considerably lower than that for the 1-sulfonic acid derivative. This means that the sulfide suppresser has a greater affinity for cytochrome c_3.

Figure 4 is a schematic view of how anthraquinones could interact with the metabolism of sulfate-reducing bacteria in order to achieve selective inhibition at very low anthraquinone concentrations observed. In this model, highly lipophilic anthraquinones partition into the cell membrane and function in a manner analogous to that of naturally-occurring menaquinones found in these bacteria, which normally participate in electron transfer coupled phosphorylation (7). In support of this we find that when 1,8-dihydroxyanthraquinone is added to a pure culture of *D. gigas* nearly all of the anthraquinone can be recovered from the membrane fraction of the organism (data not shown). We believe the anthraquinone acts as a respiratory "short circuit" by transferring electrons non-specifically throughout the cell membrane instead of the allowing electron transfer through the normal energy-conserving pathways. The consequence of this is that electron transfer no longer proceeds via energy-conserving, proton-translocating "redox loops" in the cell membrane. In the absence of efficient proton translocation, a proton gradient cannot be maintained, ATP synthesis comes to a halt, and cellular ATP declines sufficiently to inhibit the sulfate activation reaction. The sulfate-reducing metabolism may be uniquely sensitive to any loss in ATP synthesis due to the requirement for two ATPs for activation of every sulfate reduced to hydrogen sulfide. The enzyme responsible for this step is adenosine 5' phosphosulfate reductase and is found in all SRB. We have found, however, that this enzyme is completely insensitive to anthraquinone.

Due to the specific effects on sulfate respiration in *Desulfovibrio*, and the positive correlation of cytochrome reactivity with sulfide inhibition, we propose that the primary site of interaction of the anthraquinone is via oxidation of reduced cytochrome c_3. The resulting reduced anthraquinone then acts as a non-specific electron donor to the rest of the membrane-bound electron carriers.

The Treatment of Biofilms

Efficacy of anthraquinone within a biofilm is dependent upon transport of the insoluble particle to the SRB cell. Research has shown that microcolonies in a biofilm are separated by water channels through which convective flow can take place (8). The effectiveness of low dosages of anthraquinone probably lies in the material's non-reactivity with biofilm constituents. We believe that anthraquinone is transported into the biofilm, diffuses through the biofilm voids, and then diffuses or is randomly transported by Brownian motion into the bacterial microcolonies where it contacts the SRB and partitions into the cell membrane. The anthraquinone particle size is an important consideration for this process. Not only has it been shown that the anthraquinone particles need to be less than about 2.5 μm to inhibit planktonic SRB effectively (2), even smaller particles appear to be preferable for treatment of SRB within biofilms.

Figure 5 presents the results of a study in which aquarium rocks coated with a sulfide-producing biofilm were pulse-treated with either water containing anthraquinone particles (90% less than 2.0 μm) or the soluble 1,4-dihydro-9,10-dihydroxyanthracene, disodium salt. The results indicate that the ionic (soluble) form of anthraquinone was probably better able to penetrate the biofilm as compared to the particles. Visual inspection of the rocks confirmed the presence of the disodium salt in the biofilm as evidenced by a red color adhering to the rocks. While static bottle tests have shown that at comparable concentrations the anthraquinone particles will inhibit the SRB better than the 1,4-dihydro-9,10-dihydroxyanthracene salt (data not shown), the dynamic test points out the greater effectiveness of the soluble anthraquinone at biofilm penetration. It is speculated that the ionic species moves freely into the biofilm and converts to colloidal anthrahydroquinone particles due to the lower biofilm pH. (The disodium salt begins to revert to molecular 1,4-dihydro-9,10-dihydroxyanthracene at a pH less than about 10 in an anaerobic environment.) These lipophillic particles then partition into the SRB cell membrane where the anthraquinone redox process then uncouples the ATP synthesis and shuts down sulfide production.

Oilfield Applications

SRB are found in almost all oilfield production systems, especially where the waters contain sulfate. Problems associated with waters containing SRB include hydrogen sulfide generation, microbially-influenced corrosion, and solids (iron sulfides) production. Biocides, corrosion inhibitors, oxidizers, and sulfide scavengers are widely used to either control SRB growth or treat the symptoms of the SRB activity. Chemical treatments are used in seawater injection systems, including injection into the reservoir, and surface production systems, including flowlines, vessels, and tanks. Biocide treatments are typically high dose (cidal) batch injections once or twice weekly into the flowing water or mixed produced fluid streams. Regardless of the chemical, the SRB are not eliminated completely due to the difficulty for the very reactive biocide to penetrate the biofilm. Within a

relatively short duration, numbers of sessile bacteria increase to an equilibrium level as a result of growth of bacteria unaffected or not contacted by the treatment and/or repopulation by planktonic bacteria entering the system.

Anthraquinone treatments in oilfield systems inhibit SRB growth and activity. The anthraquinone penetrates into the biofilm and "coats" the substratum/biofilm surface with solid particles which are subsequently available to partition into the SRB cell membrane over a period of time, thereby increasing the likelihood of contacting all of the SRB populating the biofilm. Once the bacteria are stressed by anthraquinone, their respiration using sulfate ceases for at least several days.

A key advantage of anthraquinone over biocides is that anthraquinone is not toxic and considerably more environmentally friendly. This is especially important when treating water systems that eventually get discharged into a lagoon, river, or ocean. Also, lower and less frequent doses of anthraquinone are required to penetrate the biofilm, stress the SRB, and inhibit sulfide production, corrosion, and/or other consequences of the SRB activity. However, anthraquinone will partition into crude oil preferentially over water. Treatments of crude oil-water systems must therefore be designed properly to be cost effective. The use of a disodium salt form of anthraquinone minimizes the effects of crude oil partitioning when treating a two-phase system.

REFERENCES

1. Weimer, P. J., J. M. Odom, F. B. Cooling, and A. G. Anderson, "Anthraquinones as Inhibitors of Sulfide Production from Sulfate-Reducing Bacteria," U.S. Patent No. 5,385,842, January 31, 1995.

2. Tatnall, R. E., "Finely Divided Anthraquinone Formulations as Inhibitors of Sulfide Production from Sulfate-Reducing Bacteria," U.S. Patent No. 5,500,368, March 19, 1996.

3. Cooling, F. B., C. L. Maloney, E. Nagel, J. Tabinowski, and J. M. Odom, "Inhibition of Sulfate Respiration by 1,8-Dihydroxyanthraquinone and Other Anthraquinone Derivatives," Appl. Environ. Microbiol. *62,* 2999-3004 (1996)August.

4. Siegal, L. M., "A microdetermination Method for Sulfide," Anal. Biochem. *11*, 126-132 (1965).

5. LeGall J., D. V. DerVartanian, and H. D. Peck Jr. "Flavoproteins, Iron Proteins and Hemoproteins as Electron-Transfer Components of the Sulfate-

Reducing Bacteria," Current Topics in Bioenergetics *9*, 237-265 (1979).

6. Prince, R. C., M. R. Gunner, and P. L. Dutton, "Quinones of Value to electron-transfer studies: Oxidation-reduction potentials of the first reduction step in an Aprotic Solvent," in *Function of Quinones in Energy Conserving Systems*, 132-148. New York: Academic Press, 1982.

7. Barton, L. L., J. LeGall, and H. D. Peck Jr., "Phosphorylation Coupled to Oxidation of Hydrogen with Fumarate in Extracts of the Sulfate-Reducing Bacterium *Desulfovibrio gigas*," Biochem. Biophys. Res. Commun. *41*, 1036-1042(1970).

8. Lewandowski, Z., P. Stoodley, and F. Roe, "Internal Mass Transport in Heterogeneous Biofilms," NACE No. 95-222, presented at NACE Corrosion/95, Orlando, March 27-31, 1995.

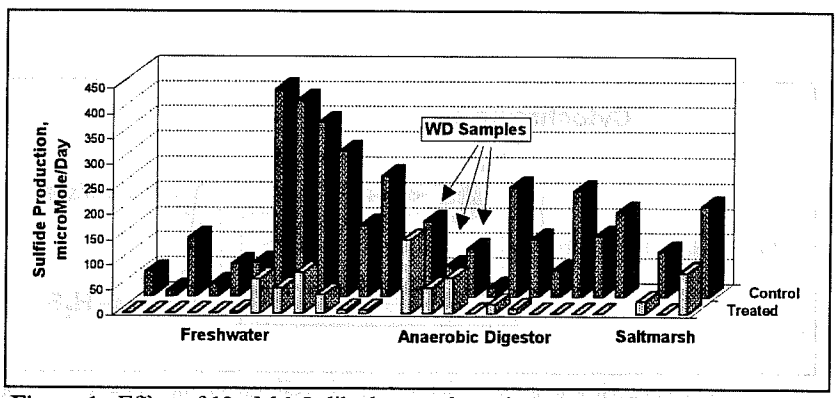

Figure 1. Effect of 12 μM 1,8-dihydroxyanthraquinone on sulfide production from crude enrichment cultures of sulfate-reducing bacteria from various environments.

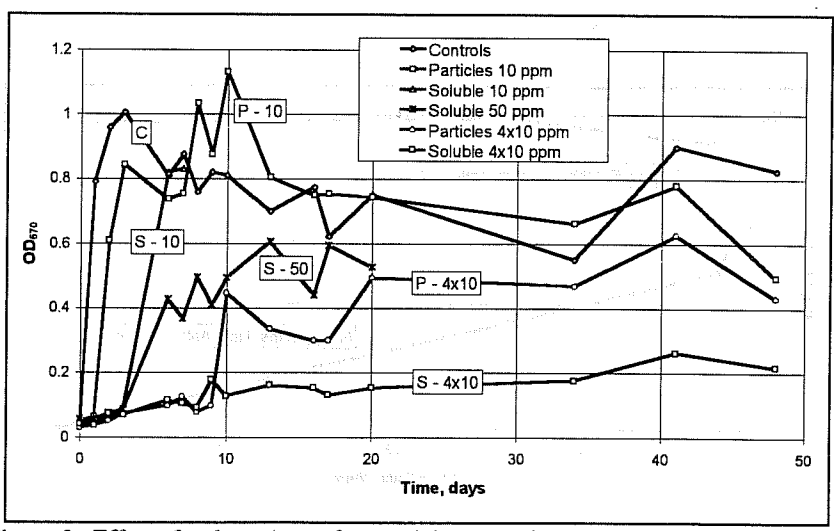

Figure 2. Effect of anthraquinone form and dosage regime on sulfide production from a mixed population of bacteria from the Prudhoe Bay, Alaska, seawater injection system. Concentrations are on basis of anthraquinone equivalent. Multiple treatments were on four consecutive days. Control shown is an average of four untreated cultures.

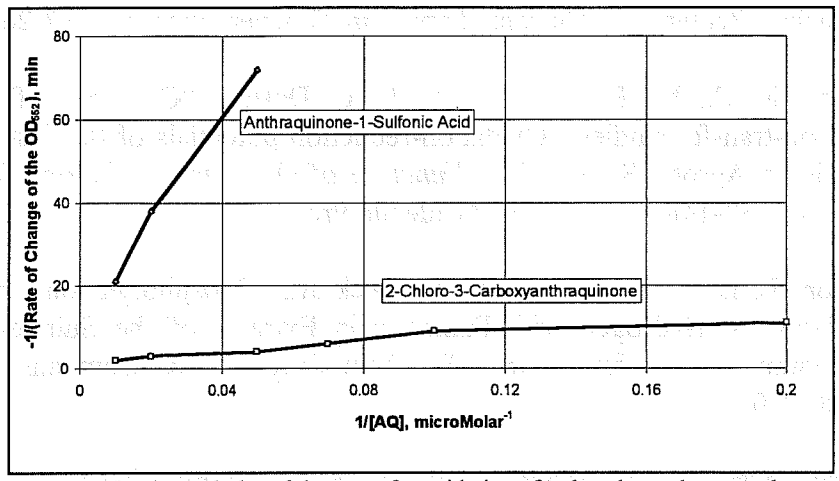

Figure 3. Reciprocal plot of the rate of reoxidation of reduced cytochrome c_3 by two anthraquinones with differing sulfide suppression effectiveness.

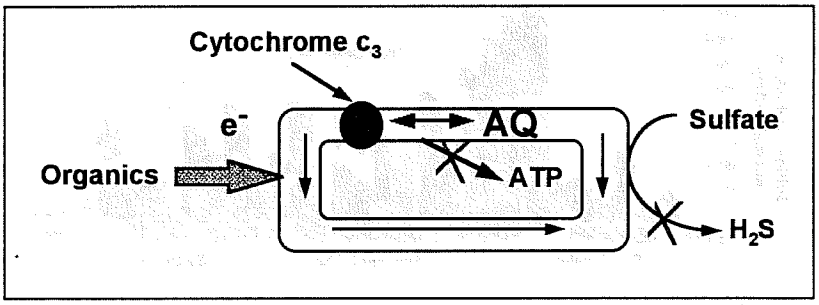

Figure 4. Schematic view of anthraquinone (AQ) in cell membrane "short circuiting" the electron transfer process, thereby halting ATP production and sulfate reduction.

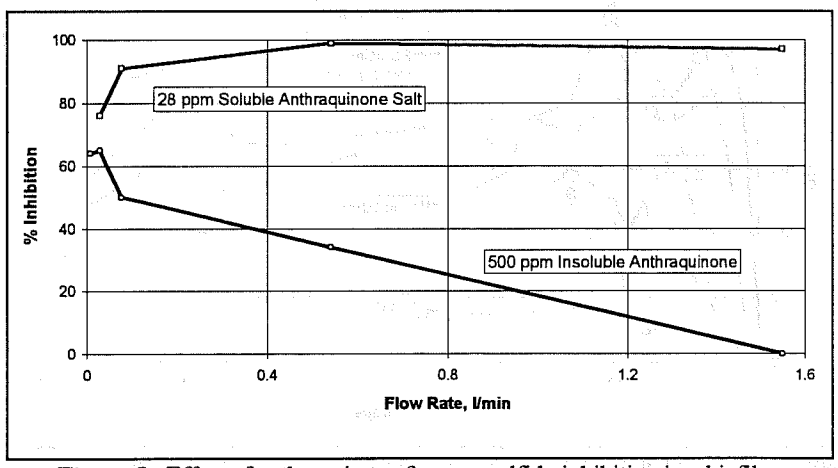

Figure 5. Effect of anthraquinone form on sulfide inhibition in a biofilm.

The Development, Chemistry and Applications of Chelated Iron Sulfur Recovery Processes

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Abstract:

The industrial use of iron as a regenerable oxidant for the conversion of hydrogen sulfide to sulfur is traced from inception as solid phase iron oxide processes to modern, homogeneous redox catalysts employing amino polycarboxylate chelated iron solutions.

Current processes contact a broad range of hydrogen sulfide bearing gas streams with a dilute, aqueous, mildly alkaline iron chelate solution using a variety of application dependent gas liquid contactors. Precipitated sulfur is continuously removed and the resulting iron (II) chelate is regenerated to the active iron (III) state by aeration in the same or a separate vessel, depending on the need to prevent admixture of air with the sweetened process gas. Process flow diagrams and both beneficial and detrimental process chemical reactions are described.

The global scope of process applications is reviewed and advantages and limitations are discussed. Future expectations based on current research are presented.

Iron, in various molecular environments, has found broad industrial application for the removal of toxic, flammable and corrosive hydrogen sulfide from a wide range of gas streams.

Chronologically, iron oxide based processes[1] were introduced around 1830 and were followed, between 1920 and 1940, by iron hydroxide slurries in aqueous, alkali metal carbonate solution[2]. Hexacyanoferrate processes[3] found limited applications during the 1930's.

Chelated iron processes were introduced in the early 1960's[4] but no successful commercial process emerged until the 1970's. Since that time, many improvements have been made in both process chemistry and plant design.

Chelated iron plant configurations can be many and varied[5] but all incorporate the basic operations of H_2S absorption, iron (II) chelate oxidation and sulfur product removal. Typical process flow diagrams are shown in Figures 1, 2 and 3. In the current process, the H_2S containing gas stream is contacted with a dilute ([Fe]=5 to 20 mM), aqueous, mildly alkaline (pH 8 to 9) homogeneous redox catalyst solution containing both amino and polyamino polycarboxylato iron (III) and a hexitol which prevents loss of soluble iron via ferric hydroxide precipitation should the solution pH rise to abnormally high alkaline values.

Reactions occurring in the absorber vessel or zone are;

$$H_2S_{(g)} + H_2O_{(l)} \rightleftharpoons H_2S_{(aq)} \quad (1)$$

$$H_2S_{(aq)} \rightleftharpoons H^+ + HS^- \quad (2)$$

$$2Fe^{3+}L + HS^- \rightarrow 2Fe^{2+}L + H^+ + S \quad (3)$$

(where L = ethylene diamine tetraacetic acid (EDTA), N-hydroxyethyl ethylenediamine triacetic acid (HEDTA), or nitrilotriacetic acid (NTA)).

Absorbers are usually custom designed in order to accommodate the large range of sour gas stream compositions ([H_2S] = 50 ppm to 100%), pressures (atmospheric to over 7MPa (1000 psi)) and flow rates (up to $65m^3.s^{-1}$ (200 MMSCFD)). Absorber devices include spray chambers, packed towers with a variety of packing, both fixed and mobile, static mixers, venturis or eductors and liquid filled columns. Series combinations are also used.

Precipitated S is continuously removed by alternative methods including sedimentation, filtration or melting under pressure.

The Fe(II)L formed in the absorber is oxidized by air in an oxidizing vessel or zone which can be integral with or separate from the absorber vessel depending on the need to avoid admixture of the H_2S free process gas with used oxidation air. Reactions occurring in the oxidizer are:

$$O_{2(g)} + H_2O_{(1)} \rightleftharpoons O_{2(aq)} \quad (4)$$

$$2Fe^{2+}L + 1/2O_2 + H_2O \rightarrow 2Fe^{3+}L + 2OH^- \quad (5)$$

thus, the overall reaction is:

$$H_2S + 1/2O_2 \rightarrow H_2O + S \quad (6)$$

The delay of almost 20 years between issuance of the first patent and the successful, large scale industrial application of chelated iron technology almost certainly stems from in-process degradation of the organic chelating agents brought about by dioxygen reduction products formed via side reactions during the oxidation of the iron (II) chelate by air according to;

$$2FeNTA^- + O_2 + 2H_2O \rightarrow 2FeNTA + H_2O_2 + 2OH^- \quad (7)$$

$$FeNTA^- + H_2O_2 \rightarrow FeNTA + OH^- + OH^{\cdot} \quad (8)$$

This early process deficiency is illustrated by data obtained using a $1000cm^3$ process chemistry simulation reactor Figure 4. Amino and polyamino polycarboxyate iron chelates evaluated and ligand to iron mole ratios were nitrilotriacetic acid, NTA (1:1 and 2:1), ethylenediamine tetra acetic acid, EDTA (1·1:1), imino diacetate, IDA (3·2:1), diethylenetriamine penta acetic acid, DTPA (1:1) and cyclohexanediamine tetra acetic acid, CDTA (1:1).

Reactor operation was conducted at ambient temperature and pressure. H_2S flow rate was held at 2.0 cm^3min^{-1} to provide a constant but unknown instantaneous concentration of hydrosulfide ions in solution. Iron concentration was 18mM. Aeration rate was $1000cm^3min^{-1}$, liquid circulation rate was $80cm^3min^{-1}$ and the pH was held between 7 and 8.

Samples were periodically removed and prepared for HPLC analysis by quantitative conversion of the iron (III) to the copper (II) chelate in order to produce a negative charge on the metal chelate as necessary to form an ion-pair with the quaternary counterion of the mobile phase. Invariably, a rapid loss of each of the above ligands was observed, Table 1.

HPLC also revealed the progressive formation of chelate degradation products. In the case of NTA, the secondary chelons, iminodiacetate, oxalate and glycinate are formed and fortunately continue to support the process before ultimately degrading to carbon dioxide, water and ammonia.

Potential chelate stabilizers such as antioxidants, buffers and free radical scavengers were screened in a series of 24 hour tests in the process simulation reactor. Several agents, particularly thiosulfate and thiocyanate anions and t-butanol, were demonstrated to remarkably increase the stability of NTA, Table 2. Thiosulfate was selected as the agent of choice based on its low cost, chemical compatibility, low toxicity, superior performance and the fact that it can be generated in-situ from H_2S when, and only when, required via the reaction;

$$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \qquad (9)$$

Control over the reaction shown in equation (9) is exercised by limiting the access of hydrosulfide anions to liquid zones containing significant dissolved oxygen contents to times when the chelon stabilizer, thiosulfate, concentration needs to be increased.

With both chelon degradation and by-product sulfur oxo-acid salt formation well under control, chelated iron processes continue to find broad application in a variety of industries.

Applications include oil refinery operations (hydrotreater off-gas, sour water stripper gas, fuel gas), oil production (enhanced oil recovery - CO_2 recycle, in-situ oil shale retorting), natural gas production (amine acid gas, direct treating), manufacturing (rayon, silicon carbide, phosphoric acid, phosphorus pentasulfide, beverage quality CO_2), odor control (biogas, waste water treating plants), and other miscellaneous areas such as geothermal power generation, coke oven gas treating and marine vessel loading. Table 3 illustrates the industrial distribution of plants[6].

Advantages of chelated iron sulfur recovery processes are ease of operation, fast kinetics, an air regenerable catalyst as opposed to a once through consumable reagent, no gas stream turndown limitations, facile and complete sulfur removal, a non-toxic, environmentally benign catalyst solution, operation at ambient temperature, and no limit on H_2S content (ppm to 100%).

Limitations include cost effectiveness up to 30 long tons of sulfur per day and a sulfur product which, although is 99+% pure, is less bright than Claus process sulfur.

With global energy requirements anticipated to increase by 55% from 1993 to 2015 and the fraction provided by natural gas expected to increase from 22% to 25% in the same period[7], the future for chelated iron sulfur recovery processes in this industry is indeed bright. This is particularly true due to the preferrential depletion of high quality reserves and the fact that future production will stem from an increasing fraction of deeper wells which generally tend to have greater concentrations of hydrogen sulfide[8].

The drive towards cleaner energy also offers new opportunities for chelated iron process applications. Lower sulfur contents are extensively mandated for motor fuels in most developed countries and will require deeper desulfurization of crudes at refineries.

Geothermal electric power generation is another active and growing application for chelated iron processes as desulfurization of the non-condensible gases (mainly CO_2 and H_2S) is required before discharge to atmosphere.

Ongoing research and development, aimed at further reductions in plant capital and operating expense, continues both at Texas A & M University and Wheelabrator's new research facility at Plainfield Illinois.

This work includes studies aimed at achieving operating cost reductions via the design and use of inherently stable chelating agents. Also, procedures to further stabilize conventional chelates are under development.

Improvements in gas-to-liquid mass transfer are anticipated to reduce the capital cost of the plant by way of smaller vessels and less expensive air blowers.

In conclusion, chelated iron processes provide and will continue to provide an economical method to remove hydrogen sulfide from gas streams containing between a few hundred pounds and 30 long tons sulfur per day, i.e. the range between quantities best treated by scavengers and the higher tonnages of the Claus process.

References

[1] Kohl, A.L. and Riesenfeld, F.C.; Gas Purification, 241-259. New York: McGraw-Hill, 1960.

[2] ibid, 283-295.

[3] ibid, 303-308.

[4] Hartley, W., Craig, R.S. and Sapiro, R.H., U.S. Patent 3,068,065, December 11, 1962.

[5] McManus, D. and Niemiec, W.J. "Chelated Iron Sulfur Recovery Processes, New Plant Installations and Research Innovations", presented at the 1996 AIChE Spring National Meeting, New Orleans, LA, February 25-29, 1996.

McManus, D. and Reicher, M. "Recent Developments in Chelated Iron Sulfur Recovery Process Technology and Chemistry", presented at the 1995 AIChE Spring national Meeting, Houston, TX, March 19-23, 1995.

[6] Nagl, G.J., "ARI LO-CAT®/ARI LO-CATII® Application and Process Technology Update" in proceedings of the 1995 Gas Research Institute Sulfur Recovery Conference, Chicago, Illinois, Gas Research Institute, 1996.

[7] U.S. Energy Information Administration, "International Energy Outlook", 1996.

[8] Thorpe, H., Oil and Water, Texas Monthly, Vol. 24(2), 88-93 and 140-145, February 1996.

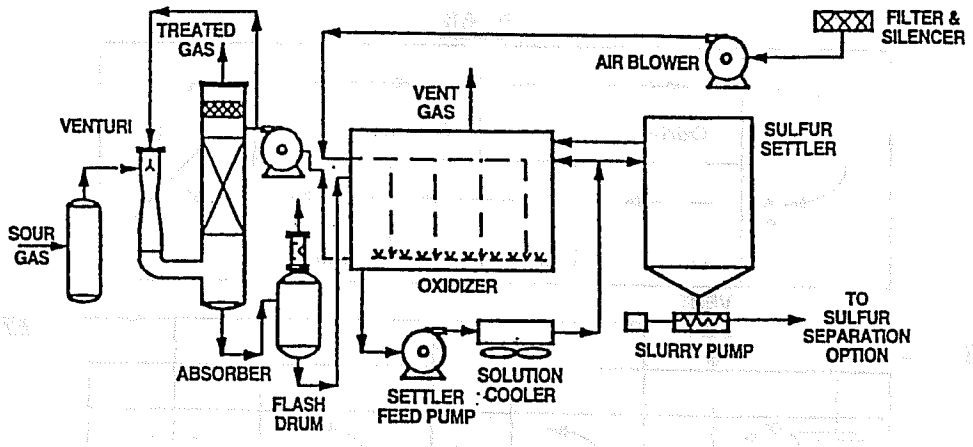

Figure 1, Process Flow Diagram, LO-CATII® Conventional Design

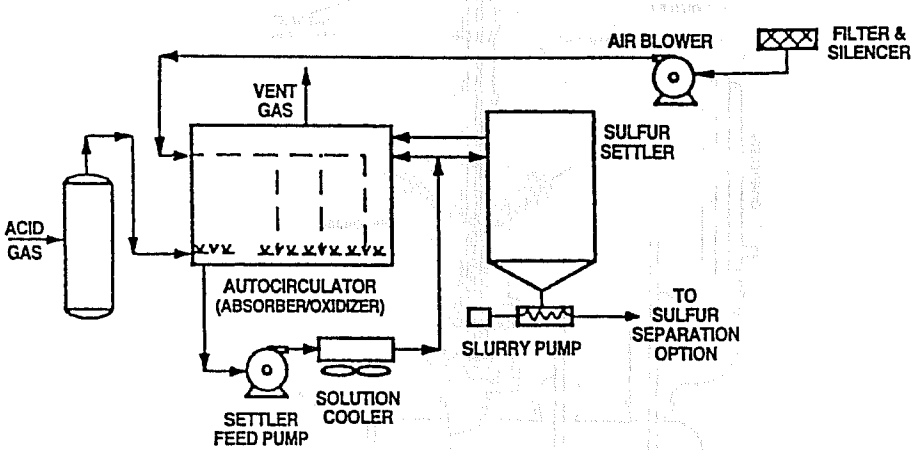

Figure 2, Process Flow Diagram, LO-CAT® Autocirculator

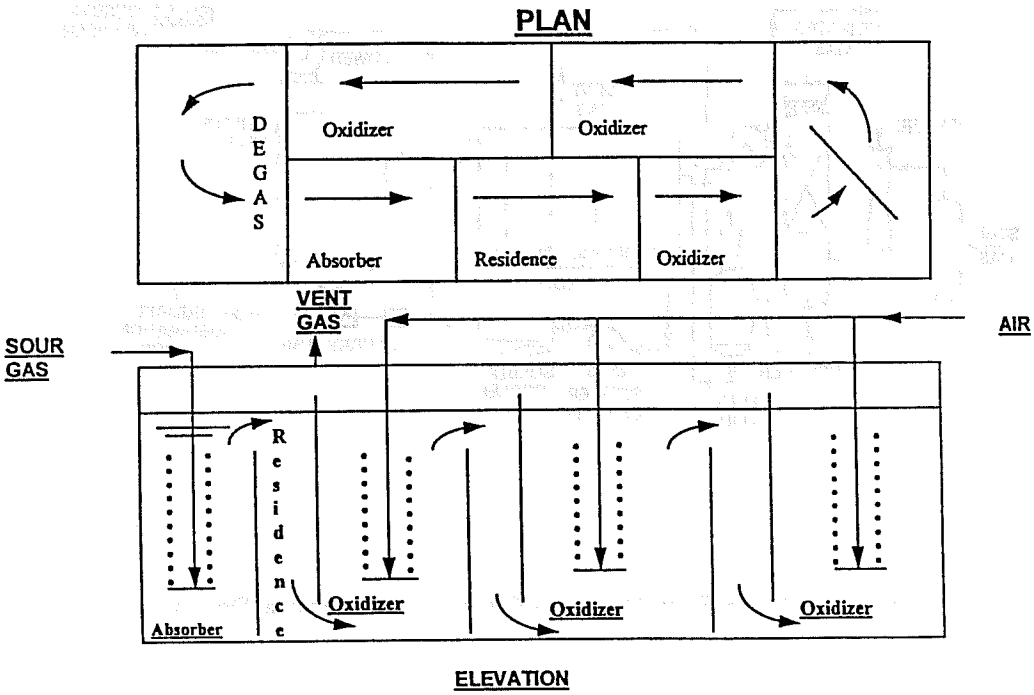

Figure 3, Schematic, LO-CATII® Autocirculator Plan and Elevation

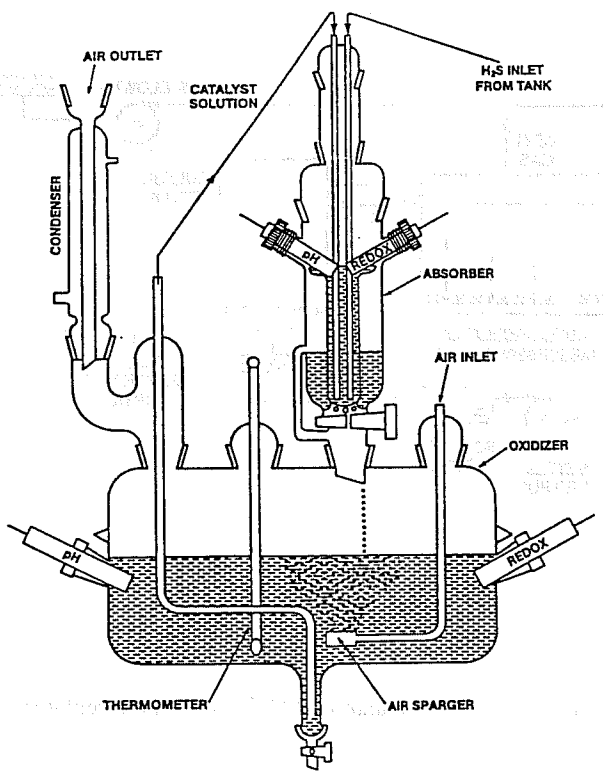

Figure 4, Process Chemistry Simulation Reactor

Table 1, Relative Degradation Rates of Iron Chelates

Ligand	Ligand to Iron Mole Ratio	Iron (mM)	Test Duration (h)	Ligand Degradation	
				1st order rate constant (h^{-1})	Ligand half life (h)
NTA	2:1	18.2	51.6	0.023	30.6
NTA	2:1	18.0	62.0	0.024	29.5
NTA	2:1	15.7	47.5	0.023	30.7
NTA	1:1	18.8	46.8	0.062	11.1
EDTA	1.1:1	18.0	19.0	0.053	13.2
EDTA	1.1:1	18.0	120.5	0.059	11.8
IDA	3.2:1	18.0	130.0	0.027	25.3
DTPA	1:1	18.8	74.0	0.070	9.9
CDTA	1:1	18.0	12.6	0.053	13.1

Table 2, NTA Stabilization by Additives, System $(NTA)_2$ Fe(II)/(III), [Fe]=18mM
*indicates no measurable degradation.

Additive	Additive Concentration ($g.L^{-1}$)	Test Duration (h)	NTA Degradation	
			1st order rate constant (h^{-1})	NTA half life (h)
NTA (NTA:Fe, 5:1)	14.8	26.5	0.0270	25.8
Ethylene glycol	100.0	26.0	0.0034	156.8
Potassium citrate	50.0	23.5	0.0110	64.5
Sodium thiosulfate	50.0	24.0	*	*
Sodium thiosulfate	50.0	92.5	0.0013	531.0
Sodium hexametaphosphate	50.0	24.0	0.0420	16.5
Sodium thiocyanate	50.0	24.0	0.0034	205.0
Sodium meta and tetra borates	25.0 each	24.0	0.0240	28.6
t-butanol	100.0	26.0	*	*
Butylated hydroxyanisole	1.0	26.0	0.0380	18.4

Table 3, Industrial Distribution of Chelated Iron Plants

Industrial Application	Number of Licensed Units	LTPD of Sulfur Capacity	Average Size LTPD
Natural Gas Processing	27	133	4.93
Misc. Processes	22	50.7	2.30
Wastewater Treatment	21	3.19	0.15
Oil Production	15	60.5	4.03
Oil Refining	12	71.61	5.97
Beverage CO_2	9	0.59	0.07
Geothermal Power	7	31.2	4.46
Chemical Reactor Vents	3	0.4	0.13
Total	116	351.2	3.03

Thermophilic Denitrifying Bacteria Isolated from Petroleum Reservoirs and the Environmental Factors that Influence their Metabolism

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ABSTRACT

Stimulation of nitrate-using bacteria by nitrate addition is an effective method in controlling microbial souring by sulfate-reducing bacteria under mesophilic conditions. However, little is known about the biological potential for nitrate reduction in thermophilic oil reservoirs. In enrichments from petroleum reservoirs in the North Sea and Alaska, we observed numerous types of metabolic activities. From freshly collected Alaskan oil reservoir production water, six anaerobic bacteria were isolated that grew optimally at 60-65°C and had maximum temperatures for growth between 78-83°C. The addition of organic acids, alcohols, carbohydrates, aromatic carboxylic acids, and hydrogen supported growth and served as electron donors for nitrate reduction. Nitrate was the only electron acceptor that could support anaerobic growth. Fermentative metabolism was not observed. In a basal salts medium with acetate and butyrate as the electron donors, large quantities of nitrate (200-350 ppm as N) were reduced primarily to dinitrogen and nitrous oxide gases, with less than 10% nitrate-nitrogen recovered as nitrite-nitrogen. Reduced sulfur compounds such as sulfide, cysteine, iron sulfide, and dithiothreitol inhibited growth by greater than 50% compared to cultures that did not receive a reduced sulfur compound. The addition of 160-320 μM sulfide to the medium resulted in a metabolic shift to the production of nitrite as the predominant endproduct of nitrate reduction. The accumulation of nitrite has been previously shown to inhibit microbial souring caused by sulfate-reducing bacteria. Thus, we have shown that denitrifying bacteria are present in thermophilic oil reservoirs, and the manipulation of their metabolism in situ to control souring may be feasible.

INTRODUCTION

The effects of oil reservoir souring, the formation of hydrogen sulfide within an oil reservoir, cost United States oil companies billions of dollars annually (1), and thus has become an important concern for the petroleum industry in recent years. There are numerous detrimental results of souring: sulfide is corrosive to metal pipelines and equipment, sulfide chemically reacts with iron to form insoluble ferrous sulfides that can physically plug the reservoir, the production of sulfide raises the sulfur content of crude oil thus increasing refining costs, and hydrogen sulfide gas is extremely toxic to humans.

Below temperatures of 80°C, the process of souring is believed to be primarily governed by sulfate-reducing bacteria (2), a group of bacteria that exhibit great metabolic diversity. These bacteria have been shown to utilize alcohols, acids, aromatics, carbohydrates, hydrocarbons, and hydrogen as energy sources while reducing sulfur oxyanions (sulfate, sulfite, thiosulfate, tetrathionate, sulfur) as terminal electron acceptors. When sulfur oxyanions are present, sulfate-reducing bacteria thrive in oil formations by utilizing carbon and energy sources such as short-chain organic acids and hydrogen within the formation, present probably from the incomplete oxidation of hydrocarbons by facultatively aerobic bacteria (3). The problem of biogenic souring is compounded when sea water, which contains 20 to 30 mM sulfate, is directly injected into petroleum reservoirs as a secondary oil recovery method (4). Unfortunately, this problem continues since the use of sea water for reservoir flooding is a common practice due to its availability and proximity to off-shore oil reservoirs.

Several methods and strategies have been investigated for the potential mitigation of microbial sulfide formation. Historically, biocides such as formaldehyde, glutaraldehyde, cocodiamine, quaternary amines, and isothialozones have been tested for antimicrobial activity against sulfate-reducing bacteria (5) and many are known to inhibit these bacteria (6). The use of biocides, however, has limited application. A problem of organic biocides is their reactivity within the reservoir, adsorbing to mineral formations, and thus limiting their dispersal throughout the reservoir and contact with the sulfidogenic microorganisms. The addition of organic biocides can also provide a source of substrate for biocide tolerant microorganisms; sulfate-reducing bacteria may benefit by directly using the biocide as a source of energy or may benefit indirectly by using the products of fermentative bacterial usage of the biocide. Another possible way to control biogenic sulfide is to eliminate the sulfate in the injection water (*i.e.* by thin membrane separation). A major drawback of these applications, in addition to limited *in situ* effectiveness, is that they are both very expensive.

A promising alternative to biocides is the use of nitrate to inhibit or control biological sulfide production. There are several possible mechanisms by which nitrate can prevent the formation or accumulation of sulfide. The addition of nitrate may shift the predominant terminal electron accepting process away from sulfate-reduction to nitrate-reduction. In this scenario, sulfide production does not occur since the nitrate-reducing bacteria effectively outcompete the sulfate-reducing bacteria for electron donors. This situation could also occur if the resident sulfate-reducing bacteria preferentially reduced nitrate instead of sulfate as the terminal electron acceptor. Thermodynamically, the Gibb's free energy change is much greater for nitrate-reduction than that for sulfate-reduction. The addition of nitrate may stimulate the metabolism of chemolithotrophic nitrate-reducing bacteria that can utilize sulfide as their energy source, thus preventing the accumulation of sulfide (7,8). Finally, nitrate-reducing bacteria may produce compounds that directly or indirectly inhibit the metabolism of sulfate-reducing bacteria. Nitrite is toxic to a wide variety of microorganisms (9). Since most sulfate-reducers are strict anaerobes, the production of nitrous oxide gas may increase the redox potential of the environment to a level that inhibits their sulfide-producing metabolism (10). Depending on the microbial populations present, any of these mechanisms or combination thereof may be operative in a given ecosystem.

Most of the previous research on sulfide inhibition by the addition of nitrate has been performed under mesophilic conditions. In this paper we report the isolation of six strains of obligate thermophilic denitrifying bacteria from a Kuparuk oil reservoir. We also report the environmental factors that control thermophilic denitrifying metabolism, and confirm the results obtained with anaerobic upflow porous column experiments in collaboration with researchers at Montana State University (11).

MATERIALS AND METHODS

Media and Conditions of culture

The composition of the basal marine medium (per liter) is as follows: 10g NaCl, 1g KCl, 0.1g KH_2PO_4, 2g MgCl, 1g NH_4Cl, 0.2g $CaCl_2 \cdot 2\ H_2O$, 1 g yeast extract, 2g $NaHCO_3$, 2 g TES (N-tris [Hydroxymethyl]methyl-2-aminosulfonic acid), 0.0005g resazurin, 10 ml vitamin solution (12), and 5 ml trace metal solution (13). A 80:20 N_2:CO_2 gas phase was used and pH was set at 7.5. Mono and divalent chloride salts were added in concentrations similar to that found in sea water.

The procedures for the anaerobic preparation and use of media and solutions were as previously described (12) The medium was dispensed into 18 x 150 mm serum tubes which were sealed with black

rubber stoppers. Additions were made from sterile, anoxic stock solutions using syringes and needles. All cultures were incubated at 62°C without shaking.

Samples were obtained from produced water obtained from the Kuparuk field on the North Slope of Alaska. To determine if heterotrophic nitrate-using bacteria were present, duplicate tubes of marine basal medium were amended with 5 mM each of acetate and butyrate as the electron donors, and about 20 mM sodium nitrate as the electron acceptor. Growth, substrate utilization, and/or product formation in the above inoculated media were compared to that observed of inoculated controls that lacked either the electron donor or the electron acceptor, or both, and to that of uninoculated controls with both the electron donor and acceptor present.

Isolation Techniques

A Kuparuk enrichment grown with acetate/butyrate as the electron donor and nitrate as the electron acceptor was serially 10-fold diluted using the basal marine medium without the addition of organic growth factors and electron donors and acceptors. Aliquots from the highest dilution tubes were streaked onto agar plates inside the anaerobic chamber. The medium used for isolation of the strains had the same composition as that used for the liquid enrichment, except 10 g/l of Gelrite gellan gum was added to solidify the medium. The plates were placed inside of a stainless steel chamber, pressurized to 10 psig with an 80% nitrogen: 20% carbon dioxide gas mixture, and incubated at 62°C. Pure cultures were obtained by repeated restreaking of well-isolated colonies on Gelrite plates until only a single colony morphology was obtained. Purity was routinely checked by microscopic observation.

Analytical Techniques

Sulfate, nitrate, and thiosulfate were measured with an high pressure liquid chromatograph equipped with a Vydac column (250 mm 4.6 mm, phase 3021) and conductivity detector.

Nitrate and nitrite were also measured spectrophotometrically using Hach assay kits.

Acetate and butyrate were measured with a gas chromatograph equipped with a flame ionization detector and a glass column packed with GP 10% SP-1200/1% H_3PO_4 matrix. N_2 and N_2O gases were

quantitated by gas chromatograph equipped with a thermal conductivity detector and stainless steel Hayesep DB column.

Sulfide was measured colorimetrically by a modified version of the methylene blue sulfide assay (12).

Growth was monitored at 600 nm by a Bausch & Lomb Spectronic 21 spectrophotometer.

RESULTS AND DISCUSSION

Six facultatively anaerobic, thermophilic, nitrate-reducing bacteria were obtained in pure culture from Kuparuk produced water. All had optimal growth at temperatures between 60 - 65°C and maximum temperatures for growth between 78 - 83°C. Nitrate was the only electron acceptor that could support anaerobic growth. The isolates metabolized a wide range of substrates for growth including organic acids, alcohols, carbohydrates, aromatic carboxylic acids, and hydrogen. Table 1 summarizes the morphological characteristics of each isolate. All strains were denitrifying bacteria because each reduced large quantities of nitrate (200 - 350 ppm as N) primarily to dinitrogen and nitrous oxide gases (Table 2).

After isolation and characterization of the denitrifying strains, we investigated the environmental factors that might influence their metabolism. The isolates were cultivated in a medium that was anoxic and reduced enough to shift the resazurin indicator from pink to clear (approx. - 50 mv). *In situ*, however, the environment may be more highly reduced, especially with an established souring population of sulfate-reducing bacteria. Figure 1 shows the growth patterns of isolates BJ-5 and BJ-6 in basal marine medium and this medium with 0.05% dithiothreitol as a reducing agent. In basal marine medium, both strains reached their maximum density within 48 hours. In medium containing dithiothreitol, however, the growth of both strains was severely inhibited, with less than one-half the growth of cultures without dithiothreitol, even after 200 hours of incubation. Inhibition of growth was also observed with other sulfur-containing reductants such as cysteine, cysteine sulfide, iron sulfide, and sodium sulfide (data not shown).

Since inorganic sulfur compounds are probably the most prevalent reductant in a souring reservoir, experiments were performed to monitor the products of nitrate-reducing metabolism in the presence of varying concentrations of sulfide. Table 3 shows the growth, amount of nitrate reduced, and percentage of nitrite formed from nitrate reduced for strain BJ-6. Without the addition of sulfide, BJ-6 reached a maximum absorbance of 0.460 and reduced 450 ppm of nitrate. Less than 10% of the nitrate reduced was recovered as nitrite under these conditions. When no organic electron donor was added, little growth occurred and the amount of nitrate reduced decreased, however, more nitrite was produced. As observed above, the addition of sulfide (160 μM - 1.6 mM)

dramatically inhibited the growth of this organism. Even though growth was inhibited in the presence of 160 μM sulfide, the amount of nitrate reduced and percentage of nitrite formed from nitrate were unaffected compared to controls that did not receive sulfide. However, with 320 μM sulfide, the percentage of nitrite formed increased drastically to 66% (296 ppm NO_2^- formed from 449 ppm NO_3^- reduced). At 1.6 mM sulfide, both growth and amount of nitrate reduced were severely inhibited, but a large amount of nitrite was produced.

These results allow us to conclude that nitrate-reducing bacteria are present in thermophilic petroleum reservoirs. In pure cultures, these organisms produced dinitrogen and nitrous oxide gases as primary products of nitrate reduction. In the presence of reduced sulfur-containing compounds, the amount of biomass formation decreased, and the products of nitrate-respiration shifted from dinitrogen to nitrite formation. These results agree well with results obtained from collaborative efforts with Montana State University. These workers found when nitrate is added to the influent of an actively souring column reactor, sulfide production was completely inhibited and significant nitrite levels were detected in the column effluent (11). Complete inhibition of biogenic sulfide is also observed with the direct addition of nitrite to the influent, suggesting that the presence of nitrite is inhibitory to the resident sulfate-reducing populations (11). Our work and that of our collaborators at Montana State University suggest that a direct addition of either nitrite or nitrate may be an effective remediative strategy to control souring in these microbial ecosystems.

REFERENCE CITED

1. Hamilton, W.A., "Sulfate reducing bacteria and anaerobic corrosion," Ann. Rev. Microbiol., 39:195 - 218 (1985).

2. Cord-Ruwisch, R., Kleinitz, W., and Widdel, F., "Sulfate-reducing bacteria and their activities in oil production," J.Petrol. Technol., 97-106 (1987) January.

3. Barth, T., "Organic acids and inorganic ions in waters from petroleum reservoirs, Norwegian Continental Shelf: a multi-variate statistical analysis and comparison with American reservoir formation waters," Appl. Geochem. 6, 1-15 (1991).

4. Rosnes, J.T., Torsvik, T., and Lien, T., "Spore-forming thermophilic sulfate-reducing bacteria isolated from North Sea oilfield waters," Appl. Environ. Microbiol. 57, 2302-2307 (1991).

5. Jack, T.R. and D.W.S. Westlake, "Control in industrial settings," 265-292, New York: Plenum Press, 1995.

6. Ruseska, I., Robbins, J., Costerton, J.W., and Lashen, E.S., "Biocide testing against corrosion-causing oilfield bacteria helps control plugging," J. Oil and Gas, 253-264 (1982) March.

7. Montgomery, A.D., McInerney, M.J., and Sublette, K.L., "Microbial control of the production of hydrogen sulfide by sulfate-reducing bacteria," Biotech. Bioeng. 35, 533-539 (1990).

8. McInerney, M.J., Wofford, N.Q., and Sublette, K.L., "Microbial Conrol of Hydrogen Sulfide Production in a Porous Medium," Appl. Biochem. and Biotech 57/58, 933-944 (1996).

9. National Academy of Sciences, "The health effects of nitrate, nitrite, and N-nitroso compounds," The National Academy of Sciences, National Academy Press, Washington, D.C. (1981).

10. Jenneman, G.E., McInerney, M.J., and Knapp, R.M., "Effect of nitrate on biogenic sulfide production," Appl. Environ. Microbiol. 51, 1205-1211 (1986).

11. Reinsel, M.A., Sears, J.T., Stewart, P.S., and McInerney, M.J., "Control of Microbial Souring by Nitrate, Nitrite, or Glutaraldehyde Injection in a Sandstone Column," J. Ind. Microbiol. submitted.

12. Balch, W.E., and R.S. Wolfe, "New approch to the cultivation of methanogenic bacteria: 2-mercaptosulfonic acid (HS-CoM)-dependent growth of *Methanobacterium ruminantium* in a pressurized atmosphere," Appl. Environ. Microbiol. 32, 781-791 (1976).

13. Tanner, R.S., "Monitoring sulfate-reducing bacteria: comparison of enumeration media," J. Microbiol. Methods 10, 83-90 (1989).

TABLE 1

Morphological Characteristics of Isolates from Kuparuk Production water

Isolate	Cell morphology	Motility	Spore type	Gram reaction
BJ-1	5 -10 μm rods	no	none	+
BJ-2	10-20 μm rods	no	terminal	+
BJ-3	10-20 μm rods	no	subterminal	variable
BJ-4	> 20 μm rods	no	terminal	+
BJ-5	10-20 μm ovoid rods	no	terminal	variable
BJ-6	> 20 μm rods	no	cyllindrical	+

TABLE 2

Nitrate Utilization by Isolates from Kuparuk Production Water

Isolate	NO_3 Utilized (ppm N)	NO_2 Detected (ppm N)	N_2O detected (ppm N)	N Recovered (%)
1	238	0	125	53
2	331	0	228	69
3	346	0	209	60
4	237	7	233	101
5	214	0	0	0*
6	214	0	0	0*

* Dinitrogen gas (N_2) was later determined to be the primary endproduct.

Cultures were grown in a basal marine media with 5mM acetate and butyrate for 14 days. Values are the mean of duplicate determinations.

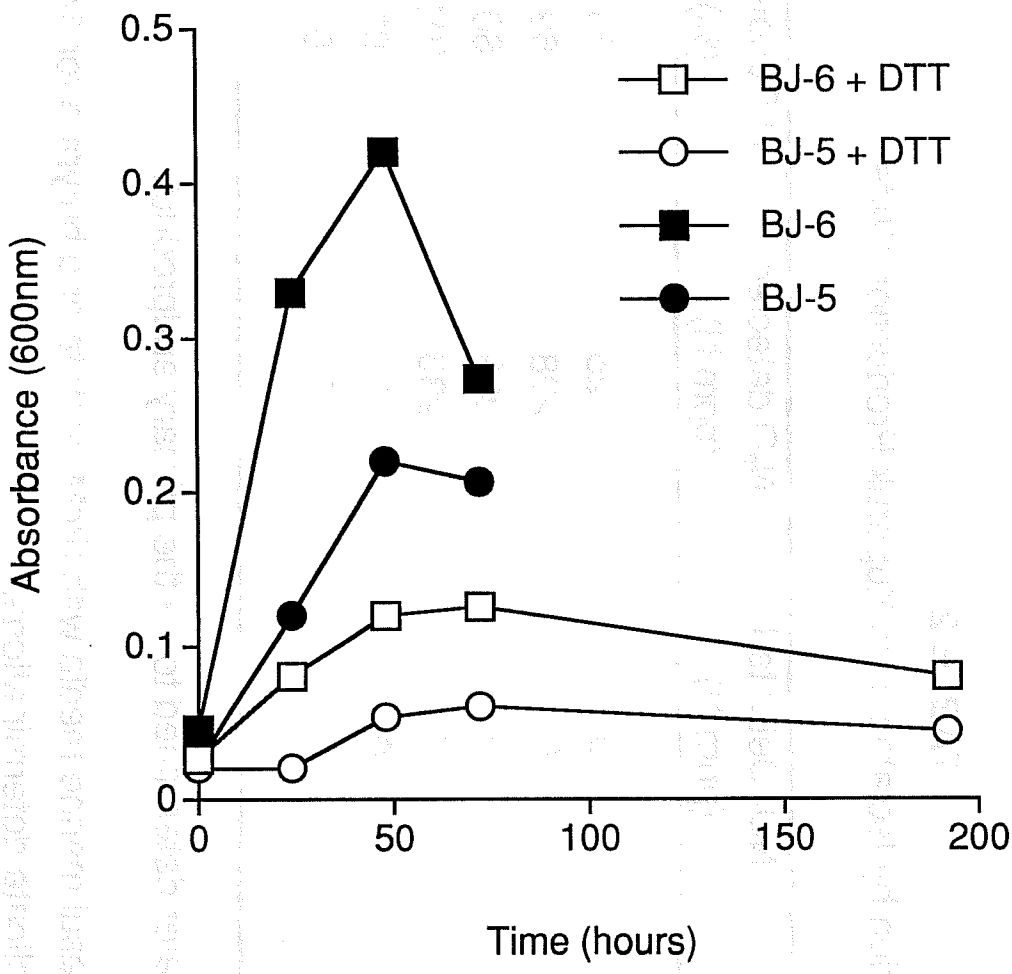

FIGURE 1 Effect of reductant on the growth of strains BJ-5 and BJ-6 in the basal marine basal medium

TABLE 3

Growth and Metabolism of BJ-6 in the Presence of Sodium Sulfide

Treatment	Max OD_{600}	NO_3^- Reduced (ppm N)	NO_2^- Formed (ppm N)	% N as NO_2^-
none	0.455	453	21	5
no donor	0.095	223	98	44
160 μM HS^-	0.278	410	30	7
320 μM HS^-	0.252	449	296	66
1.60 mM HS^-	0.105	59	21	36

Tubes contain 35 mM NO_3^- and 5 mM acetate and butyrate. Values are the mean of duplicate determinations.

Biodesulfurization of Dibenzothiophene and Crude Oil Using Electro-Spray Reactors

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Biological removal of organic sulfur from petroleum feedstocks offers an attractive alternative to conventional thermochemical treatment due to the mild operating conditions afforded by the biocatalyst. In order for biodesulfurization to realize commercial success, reactors must be designed which allow for sufficient liquid / liquid and gas / liquid mass transfer while simultaneously reducing operating costs. In this study, the use of electric field contactors for the biodesulfurization of the model compound dibenzothiophene (DBT) as well as actual crude oil is investigated. The emulsion phase contactor (EPC) creates an emulsion of aqueous biocatalyst in the organic phase by concentrating forces at the liquid / liquid interface rather than imparting energy to the bulk solution as is done in impeller-based reactors. Characterization of emulsion quality and determination of rates of DBT oxidation to 2-hydroxybiphenyl (2-HBP) were performed for both batch stirred reactors (BSR) and the EPC. The EPC was capable of producing aqueous droplets of about 5 μm in diameter using 3 W/L whereas the impeller-based reactor formed droplets between 100 and 200 μm with comparable power consumption. The presence of electric fields was not found to adversely affect biocatalytic activity. Despite the greater surface area for reaction afforded by the EPC, rates of DBT oxidation in both reactors were similar, demonstrating that the biocatalyst used (*Rhodococcus sp.* IGTS8) was not active enough to be mass transport limited. The EPC is expected to have tremendous impact upon reactor operating costs and biocatalyst utilization once advances biocatalyst development provide systems that are mass transport limited.

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Biological refining of fossil fuel feedstocks offers an attractive alternative to conventional thermochemical treatment due to the mild operating conditions and greater reaction specificity afforded by the nature of biocatalysis. Efforts in microbial screening and development have identified microorganisms capable of petroleum desulfurization (see for example *(1-7)*), denitrification *(5)*, demetalization *(5)*, cracking *(5, 8)* and dewaxing. Further investigation and manipulation of enzymatic pathways responsible for these reactions *(9)* has led to processes which are approaching commercial application, particularly in the area of biological desulfurization *(6, 10)*. Biological desulfurization of petroleum may occur either oxidatively (see for example *(2, 4, 11)*) or reductively *(1, 12-14)*. In the oxidative approach, organic sulfur is converted to sulfate and may be removed in process water. This route is attractive due to the fact that it would not require further processing of the sulfur and may be amenable for use at the well head where process water may then be reinjected. In the reductive desulfurization scheme, organic sulfur is converted into hydrogen sulfide which may then be catalytically converted into elemental sulfur, an approach of utility at the refinery. Regardless of the mode of biodesulfurization, key factors affecting the economic viability of such processes are biocatalyst activity and cost, differential in product selling price, sale or disposal of co-products or wastes from the treatment process, and the capital and operating costs of unit operations in the treatment scheme.

While significant activity is progressing in the engineering and chemical modification of enzymes so that they may function in purely organic solutions *(15, 16)*, inherent to all of the current bioprocessing of fossil feedstocks schemes is the need to contact a biocatalyst containing aqueous phase with an immiscible or partially miscible organic substrate. Traditionally, impeller-based stirred reactors are utilized for such mixing due to their ease of operation and wide acceptance in the chemical and biological processing industries. Such mechanically stirred reactors contact the aqueous and organic phases by imparting energy to the entire bulk solution, i.e. the impeller must move the contents of the reactor. Energy input in the stirred reactor is a function of the phase ratio, oil viscosity, density, reactor size, impeller speed, etc. *(17)*. Typically, impeller based reactors are capable of achieving water or oil droplet sizes of 100 -300 μm in diameter and require on the order of 1-6 W/L to do so based upon empirical correlations *(17)*. It is estimated that if impeller based systems were capable of producing 5 μm droplets, it would require ~25 kW/L *(18)*. Furthermore, no capacity exists for biocatalyst separation or emulsion breakage within the reactor. Alternative processing schemes *(10)* propose the use of "motionless mixers", in which the two phases are pumped over a reversing helical coil which creates turbulent eddies. While this method reduces the number of moving parts in the reactor, it does not reduce power requirements since costs are transferred from the impeller to the pumps required to move the liquids past the coil *(19)*.

Recent advances in the area of contactors for solvent extraction have lead to the development of electrically driven emulsion phase contactors (EPC) for efficient contact of immiscible phases *(20-23)*. In this concept, the differing electrical conductivity between the aqueous and organic phases causes electrical forces to be focused at the liquid / liquid interface, creating tremendous shear force (see for example *(24)*). This shear causes the conductive phase to be dispersed (5 μm droplet size - *(18)*) into the non-conductive phase, but does so with decreased energy requirements relative to mechanical agitators due to the fact that energy is imparted only at the liquid / liquid interface and not the entire bulk solution (see *(19)* for a review). The configuration of the EPC developed at the Oak Ridge National employs two different types of electrode regions in order to increase liquid throughput. The first, termed the "nozzle region", provides a high capacity droplet dispersion by providing an electric field with a significant vertical component. This vertical field creates the dispersion at the nozzle entrance and accelerates it into the continuous phase. A second region termed the "operating channel" employs parallel plates carrying a modulated dc offset with high voltage spikes. This signal creates an oscillating horizontal electrical field which controls the residence time of the dispersed phase and serves to continuously coalesce and redisperse the droplets as they progress in a serpentine manner through the reactor. At the base of the reactor, an electrical field exists between the electrified central plate and the grounded aqueous phase, which accelerates the aqueous droplets to the organic / aqueous interface. In this manner, droplet coalescence and hence separation on the interface is enhanced.

With the success the EPC has exhibited in the area of solvent extraction, it was proposed that it could be an efficient reactor system for aqueous / oil contacting in biorefining *(25)*. In this manuscript we assess the utility of the EPC for biodesulfurization reactions. The emulsion quality obtained in the EPC is compared to that obtained in bench scale stirred tank reactors and the rate of DBT oxidation in the two reactors is also juxtaposed. The effect of processing in the EPC on cell viability and activity is assessed, and it is demonstrated that the EPC is capable of processing crude oil as opposed to merely model organic systems.

MATERIALS AND METHODS

The oxidation of dibenzothiophene (DBT) in hexadecane was studied to investigate reactor design and performance in an easily tractable chemical system. *Rhodococcus sp.* wild strain IGTS8 (ATCC 53968) was provided by Energy BioSystems Corp. and served as the biocatalyst. Cells were supplied as a frozen paste and had a cell dry weight of 0.247 g/g of original frozen material. The aqueous phase in all experiments consisted of 0.156M, pH 7.5 potassium phosphate buffer. DBT dissolved in n-hexadecane, served as the organic phase, with typical initial DBT concentrations being 0.6 wt.%.

Liquid samples collected from the reactors were centrifuged at 14,000 RPM for 5 minutes to separate the aqueous phase and cell debris. DBT and 2-hydroxybiphenyl (2-HBP) concentrations in n-hexadecane were measured by gas chromatography using a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector as described in *(19)*. In the experiments reported here, DBT and 2-HBP concentrations in the aqueous phase were below our levels of detection. Hence only concentrations in the organic phase are reported.

Experiments conducted in batch stirred reactors (BSR) utilized 50 g of frozen *Rhodococcus sp.* wild type strain IGTS8 (ATCC 53968) cell paste which were brought up to 750 mL with 0.156M (pH 7.5) phosphate buffer and added to 250 mL of 0.6wt% DBT in n-hexadecane. The reactor vessel was a 1-L VirTis Omni-Culture fermenter, utilizing a 6-bladed Rushton-type impeller with 2 baffles. The impeller was mounted on the shaft 0.5 inches from the aerator and 2 inches from the bottom of the vessel. The reactor was kept at 30°C, agitated at 800 RPM, and aerated with room air at a rate of 0.2 SLPM.

A schematic of EPC operation is shown in Figure 1. The Teflon body of the EPC measured 10 cm x 10 cm x 61 cm. The front and rear plates of were made of clear Lexan, allowing for visual inspection of reactor operation. A thin sheet of Teflon was placed between the body and the front and rear plates to prevent wetting and current leakage to the Lexan. Three stainless steel electrodes, placed parallel to each other, measured 30 cm x 6 cm. The center electrode was charged, while the two outer electrodes were grounded. The center electrode was connected to the high-voltage electric through a supporting steel rod to avoid disturbance of electrostatic-spraying in the nozzle region. High-voltage (up to 40 kV) was generated using a pulsed DC power supply and automobile ignition parts. A power supply and two sweep/function generators were used to produce the signal which was then passed through an ignition coil to step up the signal. In order to prevent discharge of the electrodes through the circuit, a high-voltage diode was placed between the coil and the EPC. From the diode, the positively charged terminal was connected to the rings surrounding the capillary tubes, and the negative lead was attached to the center electrode. The charged rings created an initial dispersion of biocatalyst as the aqueous phase emerged from the capillary tubes. The parallel electrodes lower in the reactor enhanced droplet dispersion as the more dense aqueous phase descended to the bottom of the reactor.

In EPC experiments, the organic liquid served as the continuous phase into which an aqueous biocatalyst was dispersed. The organic phase consisted of 2,400 mL n-hexadecane containing 0.6 wt.% dibenzothiophene. The temperature of the organic phase was controlled at 30°C. Biocatalyst (26.7 g of frozen cell paste brought to a volume of 100 mL with potassium phosphate buffer) was recirculated through the reactor at 5.0 mL/min using a peristaltic pump. Aqueous phase containing the biocatalyst was sprayed into the reactor at the nozzle region, was continuously coalesced and redispersed in the operating region, and coalesced at the

base of the EPC. To better aerate, sample, and control the aqueous phase, it was circulated from the reactor base to an external reservoir at a rate of 5.0 mL/min. The liquid was then returned to the top of the reactor through two 1.6-mm-OD, 1-mm-ID capillary tubes where it was again sprayed into the hexadecane. A water bath controlled the temperature of the jacketed aqueous reservoir at 30°C. The pH was monitored throughout the experiment, and remained in the pH range of 7.0 to 7.5. In order to help alleviate possible oxygen deficiency inside the reactor, another diffuser was introduced 3 cm from the bottom of the EPC at airflow rate of 36 mL/min. Samples from the EPC were drawn hourly for twelve hours. Due to the small amount of 2-HBP production in the EPC, and hence greater associated error in GC analysis, samples were run in triplicate.

The average power consumption in the EPC was calculated as described in *(19)*. The average power consumption was found to be 7.4 W which corresponds to approximately 3 W/L and is in agreement with previously published values for the EPC *(18, 22)*. This power is significantly smaller than that needed by mechanical agitation to produce the same size droplets *(18)*.

Emulsion properties in the EPC and BSR were assessed by measuring the droplet size of the dispersed phase formed in each system. Drop size distribution in the batch stirred reactors was measured using a video technique as described in *(19)*. Drop size distributions were measured using a 3:1 ratio of buffer to organic for three conditions: 1) 750 rpm, 2) 1000 rpm, and 3) 750 rpm with 5 g of frozen biocatalyst added to the buffer. Note that under these conditions, diesel constituted the dispersed phase. *Ex situ* characterization of the EPC emulsion was conducted using a Coulter LS130 particle size analyzer. To ensure that the agitation of the sampling cell was not responsible for the emulsion measured, hexadecane (15 mL) and buffer (200 μL) were placed in the cell with 20 μL Triton X surfactant, and the size distribution of droplets was measured. The water / hexadecane emulsion from the EPC (200 μL) was then placed in 15 mL of hexadecane with 20 μL of Triton X and its size distribution was measured. Finally, to demonstrate that the instrument indeed was accurately reporting size distributions, a sample of 35 μm garnet particles was assessed under identical conditions.

Since electric fields may be utilized in some applications for sterilization *(26)*, it was desired to assess what, if any, effect the EPC has on biocatalyst viability and activity. Due to the difficulty in maintaining aseptic conditions in the EPC, plate counts of bacteria before and after operation in the EPC may be inaccurate. To directly address how the EPC may affect the activity of the biocatalyst, cells were first sprayed in the EPC, harvested by centrifugation, and then used as biocatalyst in batch stirred reactor desulfurization experiments. Resulting cell activity was compared to that of fresh cells which were never sprayed in the EPC. The EPC was operated as described above, except that rather than recirculating the biocatalyst through the EPC, 214 g of cells in 800 mL buffer were sprayed into the reactor at a

rate of 10 mL/min in a single pass. Cells were harvested through centrifugation (7,000 RPM, 30 min). A sample of recovered biocatalyst was taken to determine the dry weight of the resulting cell paste. Forty grams of this paste were placed into a batch stirred reactor containing 700 mL of buffer and 250 mL of hexadecane with 0.6% DBT. A second batch stirred reactor in which no DBT was added to the hexadecane was used as a control to account for the residual DBT and HBP which may have been introduced with the biocatalyst.

The ability to effectively create an emulsion using the EPC is a function of the densities, viscosities, electrical conductivities, and interfacial surface tension of the two phases to be mixed. Since crude oil is more dense, viscous, and potentially more conductive than the model organic liquid hexadecane (hexadecane properties: density 0.78 g/mL, viscosity 4.2 cp, conductivity 3.0×10^{-13} mho/cm, interfacial surface tension with buffer 27 dynes/cm at 21 °C), it is not known *a priori* whether the EPC is capable of creating a buffer / crude oil emulsion. In addition, due to the opaque nature of the crude oil, visual determination of EPC performance when using crude oil was not possible as it was in the hexadecane system. Crude oil was supplied by Dr. Robert G. Shong, (Texaco, Houston, TX). The oil had an API of 27, a total sulfur content of 2% and a density, viscosity and electrical conductivity of 0.86 g/mL, 42.2 cp and 2.4×10^{-10} mho/cm respectively, when measured at 21 °C. The interfacial surface tension of the oil with buffer was 12 dynes/cm at 22 °C. In order to visually assess the ability of the EPC to form an emulsion using an organic of similar density and viscosity as the crude oil, mineral oil was used as a model organic liquid. At 20°C, the mineral oil exhibited a viscosity of 235 cp, and buffer could not be successfully sprayed into the oil in the EPC due to the fact that the aqueous phase built up at the nozzle region since it did not easily fall through the viscous oil. When heated to 41 °C, the mineral oil exhibited a density of 0.86 g/L, and a viscosity of 50 cp. At this lower viscosity (still higher than the viscosity of the crude oil) successful emulsion formation was observed in the EPC. Thus, the ability to successfully spray the buffer solution in mineral oil served as a strong indicator of the ability to also spray the buffer solution into crude oil. In EPC experiments utilizing crude oil, the crude replaced hexadecane as the organic phase. All other experimental conditions remained the same as the hexadecane experiments with the exception of a water-cooled condenser added at the reactor apex to return volatilized organic species to the reactor.

RESULTS AND DISCUSSION

Diesel drop sizes which were observed in a BSR were 1) 210 ± 108 μm, n=305 for 750 rpm with no cells, 2) 188 ± 96 μm, n=309 for 1000 rpm with no cells , and 3) 118 ± 47 μm, n=323 for 750 rpm with 5 g of frozen biocatalyst added to the buffer. As expected, at higher agitation, the drop size does decrease. Furthermore, at a given agitation speed, the addition of cells decreases the droplet size significantly, indicating the presence of a surfactant agent in the biocatalyst. Drop sizes produced by agitation in the BSR were typically between 100 and 200 μm in diameter.

The results of EPC emulsion characterization are shown in Figure 2. An appreciable volume of the emulsion from the EPC consisted of droplets between 1 and 10 μm in diameter. However, most of this sample consisted of droplets between 30 and 100 μm. It is unknown whether these large droplets resulted from aqueous coalescence during sampling and analysis or if they truly represent the size distribution present in the EPC. This size distribution is thus a "worst case scenario" in that due to coalescence during the collection and sizing procedure, the actual size distribution within the reactor can said to be at least this fine. The size distribution shown for a water and hexadecane mixture agitated only by the Micro Volume Module demonstrated that the 1-10 μm emulsion seen in the EPC sample was not the result of mixing taking place in the sizing instrument since this mixing was only able to form 100 - 1,000 μm sized droplets in a water hexadecane mixture in which surfactant was also present. In addition, the size distribution shown for the 35 μm garnet particles in hexadecane demonstrates the accuracy of the instrument and the fact that the 1-10 μm droplets reported in the EPC were not the result of debris in the hexadecane.

The ability to form fine emulsions in the EPC without increasing energy utilization could have tremendous impact upon processing costs assuming that the biocatalyst utilized is active enough to be mass transport limited (i.e. the biocatalyst is so active that the rate limiting step in desulfurization is the mass transport of the sulfur bearing compound to the cell surface and not the length of time needed for reaction once the cell is in contact with the sulfur moiety). For instance, on a 1-L basis, a BSR using a 3:1 water to oil ratio and producing oil droplets of 150 μm in diameter creates $1x10^5$ cm^2 of interfacial surface area. On the same volume basis, an EPC creating 5 μm diameter aqueous droplets and having a 5% aqueous hold-up creates $6x10^5$ cm^2 of interfacial surface area, but requires $1/15^{th}$ the aqueous volume to do so. In a mass transport limited system, the rate of desulfurization would thus be expected to be 6 times as large while using 93% less biocatalyst.

The rates of 2-HBP production from DBT in an EPC run and three separate BSR runs are shown in Figure 3. Rates of 2-HBP production were within experimental variance and no appreciable difference in desulfurization rates were seen between the reactors when reported on a mg 2-HBP per gram biomass basis. Of course since the EPC treated 2.4 L of 0.6 wt % DBT with 26.7 g of biocatalyst whereas the BSR runs treated 250 mL of 0.6 wt% DBT with 50 g of biocatalyst, the change in concentration of 2-HBP in the EPC reactor was much smaller than that seen in the BSR. This small change in concentration over the reactor run accounts for the large standard deviation in the data points reported for the EPC. Desulfurization activity of the *Rhodococcus sp.* in both reactors was typically between 1 and 5 mg 2-HBP produced per dry gram of biocatalyst per hour. Note that in the experiments reported here, the only available carbon and energy source for the biocatalyst other than what may be carried over in the frozen cell paste, was hexadecane and DBT.

Other studies have utilized additional external carbon and energy sources and have reported higher activities with *Rhodococcus sp.* The rates of 2-HBP production from DBT by *Rhodococcus sp.* which had been previously sprayed in the EPC and then placed into a BSR are shown in Figure 3. The rate of 2-HBP production by these cells lies within the experimental variability seen with fresh biocatalyst. The slightly diminished activity may be attributable to loss of the initial nutrients present in the cell paste due to extraction into the hexadecane during the electro-spraying process. This initial assessment of the effect of EPC operation on cell viability and activity indicates no appreciable effect on desulfurization activity by *Rhodococcus sp.*

Aqueous phase containing biocatalyst was successfully sprayed into crude oil at 30°C using the EPC. While the emulsion could not be confirmed visually, the electrical waveforms observed form the EPC were similar to those observed during operation with hexadecane as the organic phase. While initial results have shown no measurable change in the oil's total sulfur content upon treatment in the EPC, this is not surprising due to the low catalytic ability and large volume of oil being treated. For instance, assuming a biocatalytic activity of 3 mg 2-HBP/dry gm biocatalyst per hour, one would expect the 2.4 L of crude oil's sulfur content to be reduced only from 2.000 to 1.998 after 6 hours of treatment with 26 grams of cells.

The emulsion phase contactor has been demonstrated to be an effective instrument for the creation of fine water / oil emulsions for crude oil bioprocessing. Tremendous surface area for reaction is formed in the EPC with no increase in energy consumption compared to batch stirred reactors. While the high electric fields utilized by the EPC have been demonstrated to be fully compatible with biological processing, we have been unable to demonstrate an increase in desulfurization rate in the EPC relative to batch stirred reactors due to the low activities of the biocatalyst used in these experiments. Since the current biocatalyst is not active enough to be mass transport limited, the increased surface area afforded by the EPC did not increase the observed rate of desulfurization. Despite this, the EPC is expected to be a valuable tool in the bioprocessing of oil as developments in biocatalyst performance provide commercially viable strains which are mass transport limited in batch stirred systems.

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REFERENCES

1. Finnerty, W.R.(1993),*Fuel.* 72,1631-1634.
2. Kayser, K.J., B.A. Bielaga-Jones, K. Jackowski, O. Odusan, and J.J. Kilbane.(1993),*Journal of General Microbiology.* 139,3123-3129.

3. Kim, T.S., H.Y. Kim, and B.H. Kim.(1990),*Biotechnology Letters*. 12,757-760.
4. Lee, M.K., S. J.D., and M.J. Grossman.(1995),*Applied and Environmental Microbiology*. 61,4362-4366.
5. Lin, M.S., E.T. Premuzic, J.H. Yablon, and W.M. Zhou.(1996),*Applied Biochemistry and Biotechnology*. 57/58,659-664.
6. Monticello, D.J.(1994),*Hydrocarbon Processing*. February 1994,39-45.
7. Ohshiro, T., Y. Hine, and Y. Izumi.(1994),*FEMS Microbiology Letters*. 118,341-344.
8. Premuzic, E.T., M.S. Lin, J.Z. Jin, B. Manowitz, and L. Racaniello, *Biochemical Alteration of Crude Oils in Microbial Enhanced Oil Recovery,* in *Biohydrometallurgical Technologies,* A.E. Torma, M.L. Apel, andC.L. Briarley, Editor. 1993, The Minerals, Metals, and Materials Society: p. 401-413.
9. Denome, S.A., C. Oldfield, L.J. Nash, and K.D. Young.(1994),*Journal of Bacteriology*. 176,6707-6716.
10. Dounias, G.A. and K.D. Stavropoulos, *Economic Feasibility of Biochemically Upgrading Heavy Crudes*. (1995), Brookhaven National Laboratory:
11. Kilbane, J.J. and B.A. Bielaga.(1990),*CHEMTECH*. december,747-751.
12. Kim, H.Y., T.S. Kim, and B.H. Kim.(1990),*Biotechnology Letters*. 12,761-764.
13. Lizama, H.M., L.A. Wilkins, and T.C. Scott.(1995),*Biotechnology Letters*. 17,113-116.
14. Kim, B.H., H.Y. Kim, T.S. Kim, and D.H. Park.(1995),*Fuel Processing Technology*. 43,87-94.
15. Almarsson, O. and A.M. Klibanov.(1996),*Biotechnology and Bioengineering*. 49,87-92.
16. Woodward, C.A. and E.N. Kaufman.(1996),*Biochemistry and Biotechnology*. in press.
17. Perry, R.H., D.W. Green, and J.O. Maloney, ed. *Perry's Chemical Engineering Handbook*. 6 ed. 1984, McGraw-Hill: New York. 2336.
18. Scott, T.C. and W.G. Sisson.(1988),*Separation Science and Technology*. 23,1541-1550.
19. Kaufman, E.N., J.B. Harkins, M. Rodriguez, P.T. Selvaraj, C. Tsouris, and S.E. Murphy (1996),*Fuel Processing Technology*. Submitted for Publication.
20. Kowalski, W. and Z. Ziolkowski.(1981),*Int. Chem. Eng.* 21,323.
21. Martin, L., P. Vignet, C. Fombarlet, and F. Lancelot.(1983),*Sep. Sci. Technol.* 18,1455.
22. Scott, T.C., D.W. DePaoli, and W.G. Sisson.(1994),*Ind. Eng. Chem. Res.* 33,1237-1244.
23. Thorton, J.D.(1968),*Rev. Pure and Appl. Chem.* 18,197.
24. Ptasinski, K.J. and P.J. Kerkhof.(1992),*Sep. Sci. Technol.* 27,995.
25. Lizama, H.M., T.C. Scott, and C.D. Scott, *Apparatus and Method for the Desulfurization of Petroleum by Bacteria*. (1995), United States Patent Number 5,458,752:
26. Grahl, T. and H. Markl.(1996),*Appl. Microbiol. Biotechnol.* 45,148-157.

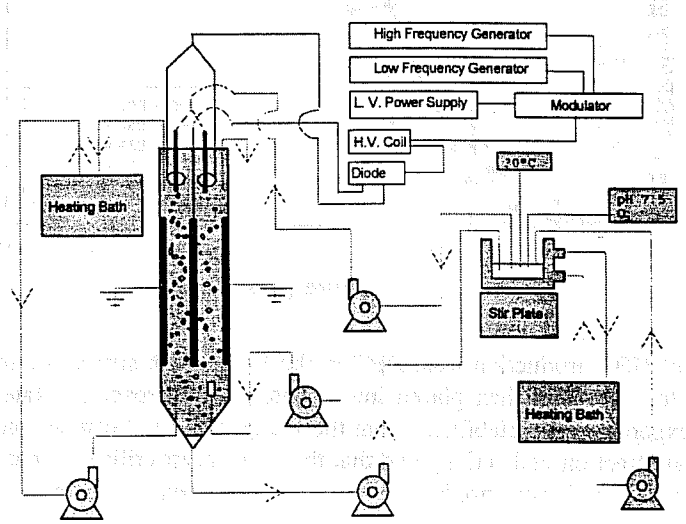

Figure 1: Schematic of the emulsion phase contactor and ancillary equipment.

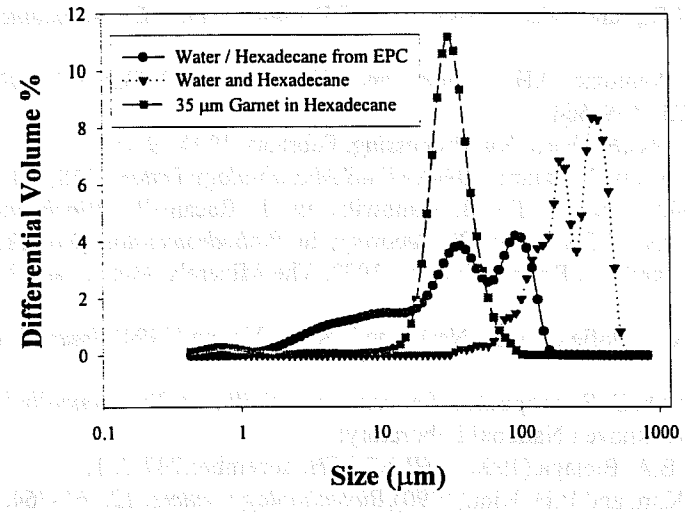

Figure 2: Characterizing the EPC emulsion using laser light scattering. The emulsion from the EPC revealed a peak owing to droplets in the 1-10 μm size range as well as peaks <100 mm presumably due to coalescence during sampling. A mixture of hexadecane and water placed in the sampling cell exhibited droplets > 100 μm in diameter, demonstrating that the sampling procedure itself was not responsible for the emulsion measured form the EPC. Finally, the size distribution for 35 μm garnet particle in hexadecane demonstrate the accuracy of the measurements and also demonstrate the small droplets seen in the EPC emulsion were not due to debris in the hexadecane used. Mean droplet sizes were 49±40, 267±121 and 34±12 μm for the EPC emulsion, hexadecane and water and garnet particles respectively.

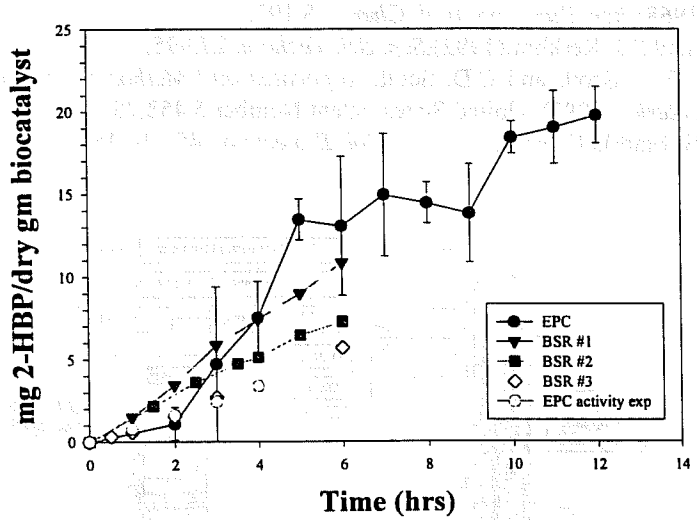

Figure 3: Rates of HBP production from DBT in the EPC, batch stirred reactors and by cells that were sprayed in the EPC and then placed into a batch stirred reactor. Rates were found to be identical within experimental variability. From these experiments it can be concluded that the EPC has no detrimental effect on cell activity and that the biocatalyst utilized is not active enough to be mass transport limited for it does not benefit from the increased surface area for reaction afforded by the EPC.

Control of Air Emissions

Application of SpectraScan® Tunable Diode Laser Instruments to Fugitive Emissions

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ABSTRACT

The advantages of lasers over broad-band light sources for spectroscopic measurements have long been recognized. Laser techniques offer the ability to measure the concentrations of trace species in a gas stream in "real time" with sensitivity and molecular selectivity not possible with broad band spectroscopic techniques. Until recently, the use of laser based instruments has been largely limited to laboratory or one-of-a-kind devices. However, the increased availability of solid-state tunable diode lasers, recent advancements in fiber optic coupling and advanced signal processing have made it possible to develop instruments that offer customers enabling technology at an affordable price. Spectrum Diagnostix has developed a family of tunable diode laser based instruments used in a variety of applications including: fugitive release detection of HF, and H_2S in refining and petrochemical industries, stack monitoring, and using extractive sample probe, in-situ process control.

SpectraScan® instruments obtain their high sensitivity and chemical selectivity utilizing a technique known as wavelength modulated spectroscopy, Described simply, a near infrared diode laser's wavelength is scanned rapidly and repeatedly through a molecular absorption line. A photodetector senses the instantaneous fraction of emitted laser power that is transmitted through the chemical bearing gas. Measurement of the relative amplitudes of off-line to on-line transmission yields a precise value of the quantity of chemical along the laser beam's path. The amplitude modulated signals are then detected using established radio receiver and signal processing techniques. The SpectraScan® monitors are designed for permanent installation in harsh industrial and petrochemical environments and are approved for Class I, Division 2 hazardous area use.

This paper describes the SpectraScan® instruments, their field applications, and reviews operating data compiled from open path measurements of HF in refineries.

INTRODUCTION

In recent years, a number of techniques have evolved for building spectroscopic instruments based on tunable diode lasers can be used to selectively measure trace concentrations of specific dangerous or undesirable gases that are entrained in a mixture of other gases.[1-4] Now, the engineering and manufacturing processes needed to develop these spectrometers into commercially available systems has been completed. A key aspect of the commercialization process has been to configure the instruments in a fashion that makes them easy to: manufacture, install permanently, use continuously and reliably, and service. We have created a family of modular instruments, called SpectraScan®, that can be configured from interchangeable components to service a specific application. These instruments monitor, record, and report low levels of gas concentrations along open lines of sight or within closed sampling cells. They are designed for installation in harsh environments, and incorporate automatic alarms, calibration, and self-health monitoring features that are critical for acceptance by users. Standard interfaces are available for remote communications with other plant monitoring or control equipment.

Applications include: open-path sensing of fugitive hazardous compounds affecting worker safety around production areas or pipe lines, and trace contaminant monitoring in chemical streams permitting precise process control.

BACKGROUND

SpectraScan® monitors rely on well-known spectroscopic principles coupled with recent advances in diode lasers and optical fibers developed by the telecommunications industry and a newly-perfected detection technique called wavelength modulated laser absorption spectroscopy.[5, 6] All gas molecules absorb energy at specific wavelengths in the electromagnetic spectrum, thus providing a unique absorption signature for that chemical. At wavelengths slightly different than these absorption lines there is essentially no absorption. By passing a beam of light through a sample of the target gas, tuning the beam's wavelength to one of the target gas's absorption lines, and accurately measuring the absorption of that beam, one can deduce the concentration of target gas molecules integrated over the beam's path length. This measurement is usually expressed in units of parts per million-meter (ppm-m).

The tunable diode lasers (TDLs) used in SpectraScan® serve as the wavelength-selectable light source. They are solid-state lasers, packaged with thermoelectric coolers and thermistors that permit the laser temperature to be regulated with an accuracy better than 50 mK. Accurate control of the electrical current supplied to power the laser permits precise selection of the laser

wavelength. The laser linewidth is considerably narrower than molecular absorption linewidths. These combined features provide the means for tuning the instrument to a specific molecular absorption line which is selected to be free of interfering absorptions from other molecules. The center wavelength is also continually scanned across the selected absorption line. While this scanning, occurs, the fraction of emitted laser power that is transmitted through the gas mixture. is monitored with a photodetector. When the wavelength is tuned to be off of the absorption line, the transmitted power is higher than when it is on the line. Measurement of the relative amplitudes of off-line to on-line transmission yields a precise value of the target gas concentration along the path transited by the laser beam. In SpectraScan®, the laser wavelength is scanned across the absorption line roughly two million times per second, causing the detector to generate a signal that contains a 2 MHz amplitude modulated voltage. This signal is detected using established, highly sensitive, signal-processing techniques while remaining free of interfering signals from external radio, light or heat sources. Thus, the tunable diode laser spectrometer offers a combination of sensitivity and freedom from cross-sensitivity to other molecules that, for many chemicals of interest, is not otherwise available.

SpectraScan® instruments use proprietary hardware and software to operate in two measurement modes concurrently. In the "normal" measurement mode, the high-sensitivity capability described above is utilized to continually monitor low gas concentrations with a nominal one second time constant. The dynamic measurement range in the normal mode is about 1000:1. The minimum sensitivity is typically 1 ppm-m, depending on gas species and system configuration. The "event" mode is less sensitive than the normal mode, but responds more than 100 times faster. Its purpose is to assure detection of response to catastrophic events which may form a cloud that obscures the laser beam's path. For example, the event mode will detect the leading edge of an HF cloud and activate appropriate alarms within one second of detection.

The lasers by early developers of the wavelength modulation detection techniques relied on liquid nitrogen cooling for thermal stability. The liquid nitrogen needed to be replenished frequently by a human operator, thus limiting the continuous use of these devices in hazardous environments. The laser packages that we use were developed by and are marketed primarily for the telecommunications industry, which demands continuous, reliable, unattended operation. These lasers generate light at near-infrared wavelengths and are readily coupled to optical fibers, making possible long-distance transmission of the laser beam. The lasers, along with their associated electronics and microprocessor, therefore can be located remotely from harsh or hazardous measurement areas.

The laser beam used by each SpectraScan® monitor originates in a control console that may be located up to 1 km from the measurement path. The laser beam is brought via optical fiber to the beginning of the measurement path, the

beam exits the fiber and is transmitted into the gas bearing the target species. At the opposite end of the measurement path, the laser beam impinges upon a photodetector, where the information it carries is converted into an electrical signal. The electrical signal is returned to the electronics console via coaxial cable. At the console, the signal is processed and the path-integrated target gas concentration is reported. Each console can service up to four measurement paths, which may be of either the "Open-Path" or "Process Control" configuration.

Open-Path Configuration

The open-path instruments transmit an eye-safe laser beam along a line of sight up to 200 meters in length. A typical open-path installation is illustrated by Figure 1. An optical transceiver is securely mounted at one-end of the path, and a hollow corner-cube type retroreflector is mounted at the opposite end. The control console is typically located in a control room or similar benign environment. The transceivers are certified for installation in Class I, Division 2, Groups B, C, and D classified hazard environments, where hazardous concentrations of flammable gases or vapors may be present due to intermittent abnormal operating conditions. The transmitter portion of the transceiver is aimed during installation to direct the eye-safe laser beam onto the retroreflector which redirects the beam back to the receiver section. The transceiver design passively separates the transmitted beam from the received beam, and focuses the received beam onto the photodetector.

Process Control Probe

The SpectraScan® Process Control (PC) monitors employ the same basic control console, but measure target gas concentrations within closed multi-pass optical cells installed in measurement chambers through which the gases of interest are continuously drawn. One version of this configuration incorporates a Herriot-style optical cell that is installed within a low-pressure chamber. In the Herriot cell, the laser beam is reflected between a pair of mirrors many times before emerging from the cell and striking the photodetector. In our cells, the laser beam transits the 25 cm cell length 40 times, thus providing the sensitivity of a 10 m optical path. The Herriot cell design is athermal and optically stable. They are installed in measurement chambers of one liter volume. By operating the chambers at low pressure (<0.25 atm) rather than atmospheric pressure, the gas exchange rate is increased, thereby enhancing the instrumental response time, and the spectroscopy is simplified by reducing absorption line widths and making more absorption lines accessible with freedom from interference by nearby absorption lines of other gas species.

System Console

The SpectraScan® System Console comprises a number of modular components, as illustrated by Figure 2. Each module performs a specific function, and the specific sub-modules used in any particular instrument depends on the gas

being monitored and the number of measurement paths used The modules include:

- *Control Console module* comprises:

  Laser transmitter submodule including a tunable diode laser plus its drive and control electronics.

  Reference cell containing a small amount of the target gas and providing a feedback signal used to lock the laser wavelength to the target absorption line.

  Analog signal processors that extract the absorption signal information from each detector's output and converts it to a format suitable for analysis by an embedded digital computer/controller.

  Signal analyzer and *system controller* submodules that interpret the processed absorption signals and provides appropriately formatted outputs. The *system controller* also monitors and stores system operating parameters, facilitating start-up and permitting automatic identification of system problems.

  User interface which provides visual indications of measured gas concentrations and any abnormal operating conditions.

- *Power supply module* that is configurable to convert all worldwide AC power standards to the dc voltages needed to operate the other modules.

- *System interface module* that houses relays indicating system status and connections between the relays, 4-20 mA concentration output, and serial digital outputs to other equipment. These signals can be used to activate alarms or to automatically initiate emergency procedures.

- A *temperature control module* houses a pair of PID controllers for each extraction probe. (Heated extraction probes only.)

These modules are intended for installation in a 19 inch rack. Optional System Console housings include NEMA rated enclosures as needed to suit its installation environment. Air-purging for enclosures is available.

APPLICATION

Open path monitoring at oil refineries.

Toxic chemicals, such as Hydrogen Sulfide (H_2S) and Hydrogen Fluoride (HF) are used or produced as by-products at many refineries. Though normally not released to the atmosphere, refinery operators want to continuously monitor areas near storage areas, pipelines, and processing sites to detect and correct small leaks of these hazardous gases before they become serious problems.

SpectraScan® is used in an open path configuration to meet these needs. A laser beam is projected from one of the system's transceivers to a remotely located retroreflector. The SpectraScan® system then reports the amount (expressed as ppm-m) of the gas species being monitored along the path. The minimum sensitivity for HF measurement is about 0.2 ppm-m, and for H_2S, about 5 ppm-m. These units can be interpreted as meaning that a one meter diameter cloud containing 5 ppm of H_2S would be detected by SpectraScan®. This detection limit can be contrasted with accepted exposure standards of 20 ppm over an 8 hour period. At concentrations of a few hundred ppm, H_2S can no longer be smelled and is lethal in a few minutes. Thus the sensitivity offered by SpectraScan® is more than adequate to help assure safe working conditions. Similarly, the accepted safe 8 hour exposure to HF is 3 ppm, well above SpectraScan's® minimum sensitivity.

We have found SpectraScan® to be useful for monitoring very low levels of ambient HF that are present during normal refinery operations. For example, the sensitivity of 0.2 ppm-m translates into a sensitivity of 2 ppb distributed uniformly over a 100 m path. This exquisite sensitivity to low average concentrations is now being used to help refinery operators contain previously undetected emissions. A SpectraScan® Open Path Monitor has been operating continuously within the HF alkylation unit of a North American refinery since July 1995. The instrument was configured with two measurement paths, each about 80 m long. Some typical data acquired by this instrument over a 24 hour period on a late-summer day are shown in Figures 3 through 5.

Figure 3 shows a voltage proportional to the laser power received at each detector. Although there are some insignificant gradual variations in the received power, due primarily to small movements of the transceiver on its mounting post, this figure shows that the laser beam was transmitted and received essentially continuously throughout the recorded period. The short-lived interval where the laser power on Path 1 drops to zero is called a beam block, and is the result of refinery workers walking in the beam's path. SpectraScan® automatically recognizes beam blocks and, when one occurs, it freezes the blocked path's reported concentration at the last known value, instead of updating the data stream. It also activates a warning that communicates the blocked condition an LED indicator on the User Interface Panel and closure of a relay in the System Interface module.

Figure 4 shows some of the internal system signals that are continually monitored to assure that the instrument is operating properly. These signals include: the laser drive current (Current), the laser temperature (Temp), the output of a photodiode that monitors the laser's output (Photo), the ambient temperature of the control console (Backplane), and the current required to operate the thermoelectric cooler that maintains the laser temperature (TEC). This figure simply shows that these signals are all within their normal operating range and change little over the reporting period. The combined data of Figures 3 and 4 assure us that the instrument is operating normally.

Figure 5 shows the HF concentration reported along the two paths during this period. (Note that these data were selected from months of daily traces specifically to make this illustration). The data are characterized by a typical low concentration of a few ppm-m, which translates into an average ambient concentration of a few tens of ppb, well within accepted safety limits. (Note that the zero points of the two data sets have been offset from each other for clarity.) HF emissions greater than the usual ambient are seen for two periods in these data: First a period lasting about 90 minutes, and later a short-lived "spike". Path 1 shows higher concentrations because of wind direction. The 90 minute emission was caused by maintenance work on a pump in the alkylation unit. The spike was attributed to a specific plant maintenance operation that was previously believed to not cause any HF release, because the release was too small to be detected by other instruments. Plant operations have since been modified to minimize releases from that type of operation.

CONCLUSION

The main advantages of this technique over competing optical monitoring methods are the sensitivity, immunity from interferences, and speed of response. In addition, the instruments are robust, reliable, and cost effective. There are no moving parts, and delicate electronic components can be located in benign environments while being connected via rugged optical fiber to measurement paths located in harsh or hazardous areas.

Of course, all optical techniques offer significant advantages when compared to non-optical sensors in many applications. Open-path measurements like those described herein are possible only optically. Optical measurements are generally non-intrusive, that is, they do not interact with or perturb the sample being measured. For these reasons, we look forward to explosive growth in the use of tunable diode laser monitors for chemical sensing, now that these instruments are available commercially.

REFERENCES

1. M.B. Frish. "The SpectraScan® Family of Trace Gas Monitors based on Tunable Diode Laser Spectroscopy", AWMA Paper No. 96-TP26B-05, (June 1996), and references contained therein.

2. H.I. Schiff, D.R. Hastie, G.I. Mackay, T. Iguchi, and B.A. Ridley, "Tunable diode laser systems for measuring trace gases in tropospheric air," Environ. Sci. Technol., 17:352A (1983).

3. D. Bomse, "Diode Lasers: Finding Trace Gases in the Lab and the Plant," Photonics Spectra, 29(6):88 (1995).

4. D.E. Cooper and R.U. Martinelli, "Near-infrared diode lasers monitor molecular species," Laser Focus World. (Nov, 1992).

5. D.E. Cooper and C.B. Carlisle, "High-sensitivity FM spectroscopy with a lead-salt diode laser," Opt. Lett., 13:719 (1988).

6. D.S. Bomse, A.C. Stanton and J.A. Silver, "Frequency Modulation and Wavelength Modulation Spectroscopies: Comparison of Experimental Methods Using a Lead-Salt Diode Laser," Appl. Opt., 31:718 (1992).

7. ----, "New HF detector accepted for use by refining consortium", Oil and Gas Journal, 94(8), 46 (1996).

FIGURES

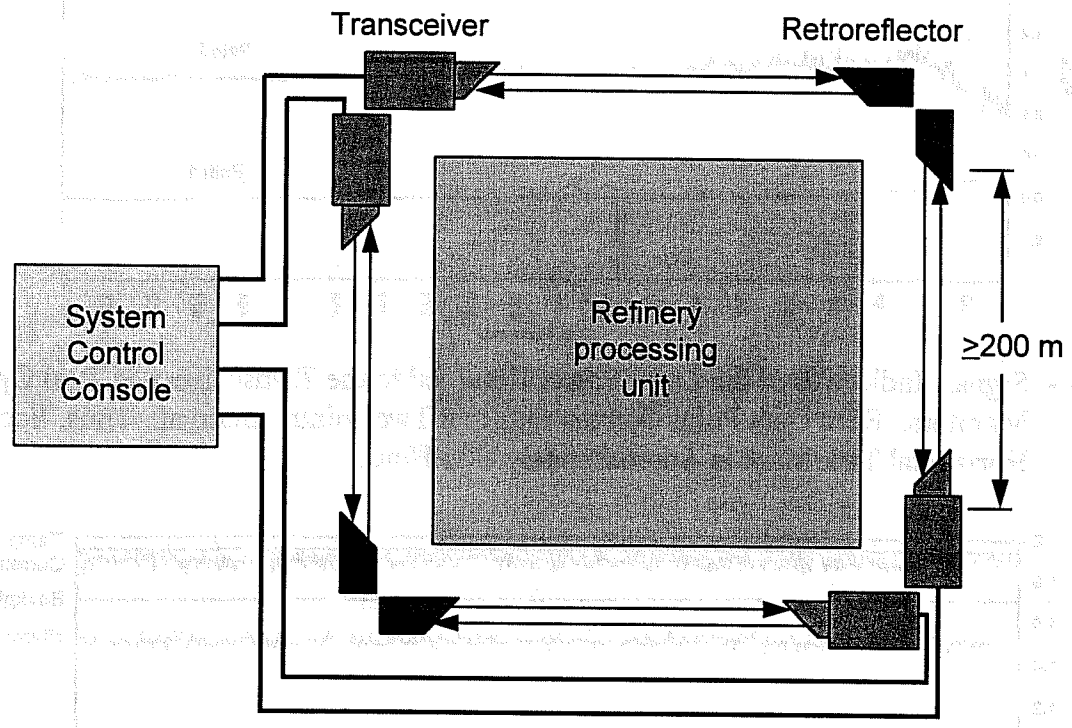

Figure 1 - SpectraScan® Open-Path Monitor field configuration.

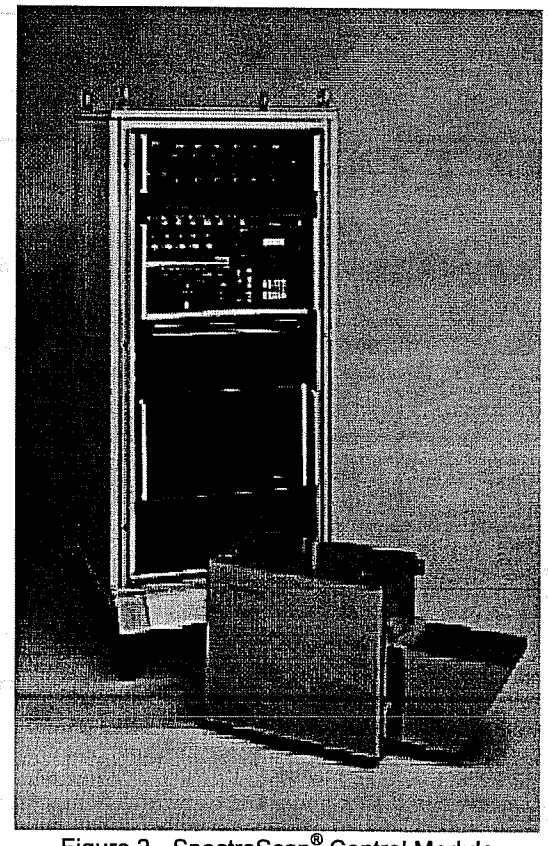

Figure 2 - SpectraScan® Control Module

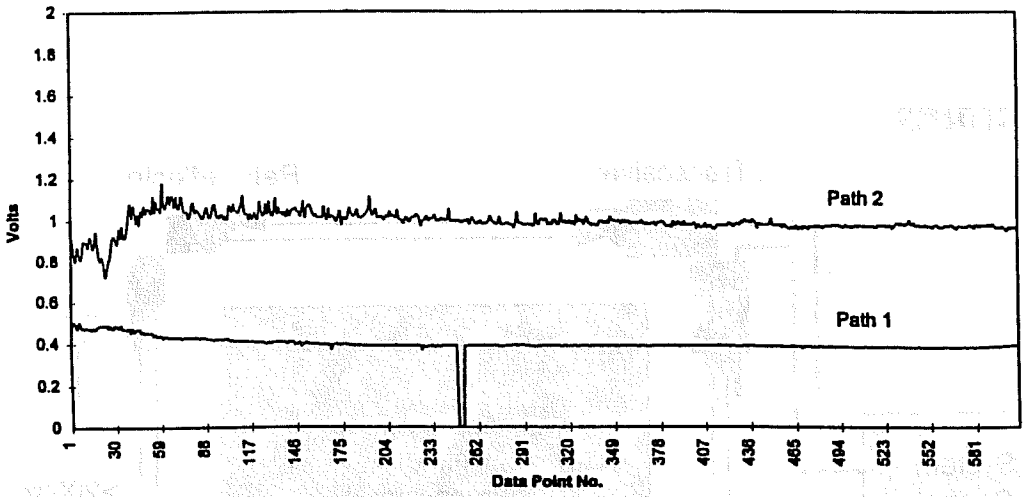

Figure 3 - Signals Indicative of the Laser Power Returned to the Transceivers of Two Open-Path Monitors. Each Data Point Corresponds to a Two-minute Interval. Thus, Each Horizontal Tick Mark is Approximately One Hour.

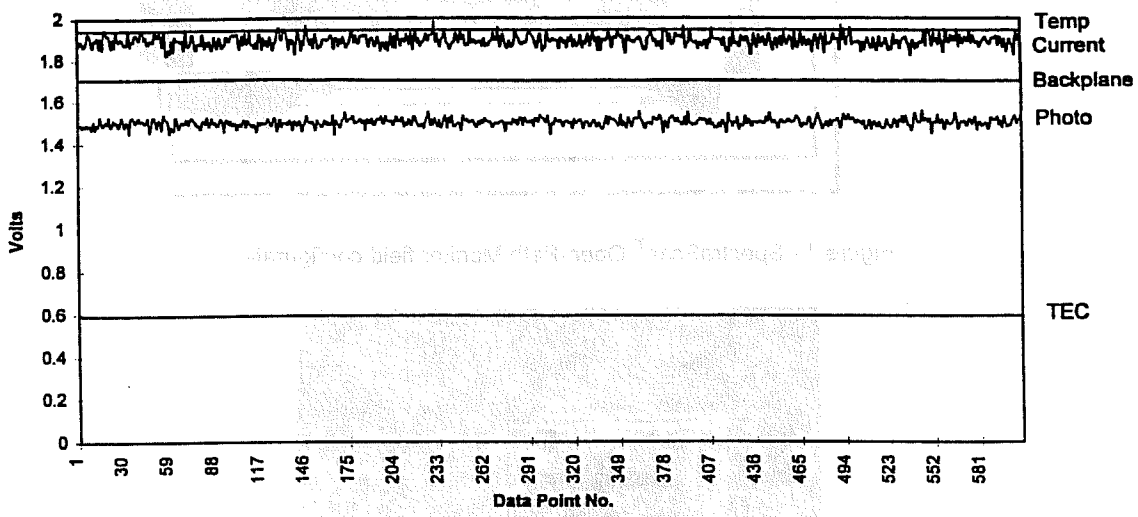

Figure 4 - Internal Control Module Signals Indicative of Normal System Operation

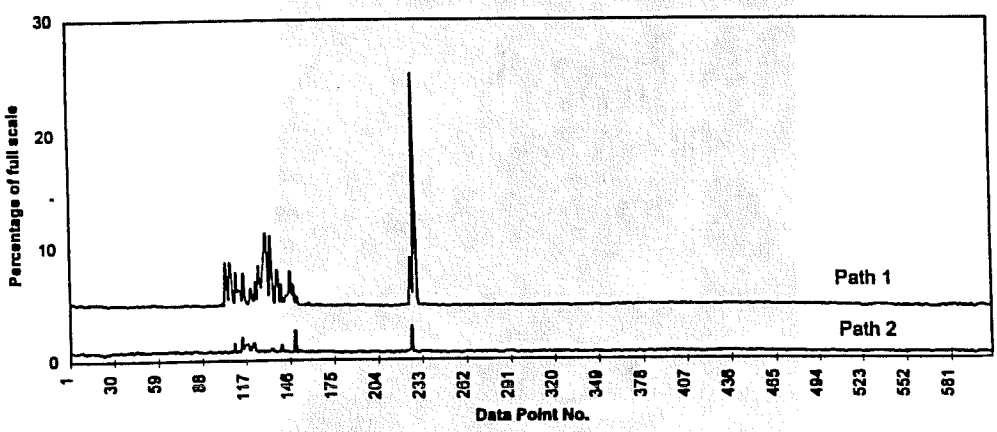

Figure 5 - Relative HF Concentrations Measured Along the Two Paths

Air Emissions Control Using Zeolitic Materials

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Abstract:

Natural zeolites are abundant and inexpensive minerals; their commercial applications include water pollution control, water purification, and reaction catalysis. However, it appears that natural zeolites have not been extensively studied in the context of air emission control. The research presented here is a lab-scale evaluation of the potential use of zeolites to remove organic compounds (e.g. BTEX) from a gas stream.

This research indicates that natural zeolites are able to separate benzene and o-xylene from a gas stream. This separation is effective at low temperature (ca. 100° C), and is reversible at high temperature. We hypothesize that zeolite impregnated with potassium permanganate will be able to separate BTEX from a gas stream, and allow sufficient time for the organics to be oxidized by the potassium permanganate.

The properties of zeolites which are important in pollution control applications include large surface area, small pore size, and large cation exchange capacity.

INTRODUCTION

This paper reviews the properties and uses of natural zeolites, and proposes a new application for the separation and chemical oxidation of aromatic hydrocarbons from a gas stream. Some preliminary results are presented, which indicate that the separation step is feasible.

A. Review of Natural Zeolites

Natural zeolites are a class of microporous aluminosilicate minerals, composed of crystalline arrangements of $[SiO4]^{4-}$ and $[AlO_4]^{5-}$, various cations, and water of hydration. The $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra are bonded with Si-O-Si and Si-O-Al. The general formula of zeolites is $(MN_2)O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O$, where M can be Mg, Ca, Sr, or Ba, and N can be Na or K (1). The substitution of an $[AlO_4]^{5-}$ for a $[SiO_4]^{4-}$ results in the formation of a negatively charged site in the structure. Cations present in the synthesis mixture occupy these charged sites. Water molecules occupy the cavities and channels in the zeolite structure. The location and amount of water in a given zeolite depends on its structure, and the number and type of cations in the crystalline structure (2).

In general, natural zeolites are formed by reaction of alkaline saline solutions with volcanic glasses, tuffs, silica, or clays. Formation of zeolites can occur in conditions ranging from low to moderate temperature, low to high pressure, and high salt concentration. Zeolites may be found as crystal inclusions in volcanic rocks, and as massive deposits in sedimentary and low-grade metamorphic rocks (2). Chabazite, clinoptilolite, and mordenite are the three most common natural zeolites. Zeolite deposits are widely distributed around the world; there are currently seven producers in the United States, with a combined annual production of about 10,000 tons in 1988 (3), and 55,000 tons in 1995 (4).

The three-dimensional structure of any given natural zeolite depends on the proportions of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ in the structure. Each Si and Al atom is bonded with four oxygen atoms, in a tetrahedral geometry. All of the oxygen atoms in the structure are shared between Si and/or Al atoms. As a result, the

ratio of (Si + Al) to O atoms is always 1:2. However, the Si:Al ratio, and number and location of water and cations sites, varies with different zeolites. The arrangement of the $[SiO_4]^{4-}$, $[AlO_4]^{5-}$, and cations create cavities and channels, in which cations and water molecules are located. The diameter of these cavities and channels is on the order of 3 to 8 Å. The size of the channels can vary, depending on the cations that are in the structure. Divalent cations are typically smaller than monovalent cations. Consequently, zeolites with divalent cations have slightly larger channels. Some properties of the natural zeolites used in this study are summarized in Table 1.

Zeolites can be characterized by their dehydration behavior. Some zeolites can be dehydrated with no major structural changes, while others exhibit major structural change upon dehydration (5). This structural collapse can be reversible or irreversible, depending on the specific zeolite, and the conditions under which dehydration and rehydration occur. The products used in this study consisted of clinoptilolite and mordenite, whose structures are stable to 750° C and 800° C, respectively (5).

Zeolites can also be characterized by secondary building units (sbus), which are the simplest structures which completely describe a zeolite framework. There are eight distinct sbus, ranging in complexity from a four-atom ring, to a complex nine-atom unit. The three different sbus found in the natural zeolites used in this study are shown in Figure 1.

Clinoptilolite is formed by the bonding of 4-4-1 units in a layer arrangement. The bonding of the layers results in two distinct channels bounded by eight oxygen atoms, and one channels bounded by ten oxygen atoms. These channels are also called oxygen windows. The diameters of these windows are 4 x 5.5 Å, 4.1 x 4.7 Å, and 4.4 x 7.2 Å, respectively (6).

Mordenite is composed of 5-1 units linked together in a series of chains. Two channels are found in the mordenite structure, one bound by eight-ring oxygen windows, the other by twelve-ring oxygen windows. The dimensions of these windows are 2.9 x 5.7 Å, and 6.7 x 7.0 Å, respectively. There are eight cation and water sites in the mordenite structure (2).

B. Review of Permanganate Oxidation

Potassium permanganate has long been used as an oxidizing agent. It has been used extensively for synthesis of organic chemicals. It effectively oxidizes toluene, xylenes, phenol, alkenes, alkyl side-chains, acids, alcohols, organo-sulfur compounds, and organo-nitrogen compounds. The oxidation of some of these compounds is incomplete, leading to the formation of partially oxidized organics such as ketones and organic acids (7 ,8). There are some applications in which permanganate is used to oxidize gases. Aqueous permanganate solution has been used as an absorbent to treat malodorous gases (7). Zeolites impregnated with potassium permanganate can be used to oxidize ethylene gas at ambient temperature conditions (9, 10).

C. Uses of Natural Zeolites

The properties of zeolites lend themselves to several kinds of unit operations and processes. The combination of small pore size, cation exchange capacity, large internal surface area, thermal stability, and structural integrity. Zeolites are widely used as petroleum cracking catalysts, molecular sieves for the separation of gases, desiccants, and ion exchange media.

MATERIALS AND METHODS

A. Instrumentation

The primary analytical instrument used in this research was a Hewlett Packard model 5730 gas chromatograph (GC). The GC was equipped with a flame ionization detector (FID). Nitrogen was used as the carrier gas, and hydrogen and compressed air were used as the FID fuel and oxidizer, respectively. Gas pressures were regulated with standard gas cylinder regulators. Gas flow rates were measured at the detector, with a soap film flowmeter. Hydrogen and compressed air flow rates of 54 and 162 mL/min, respectively, were used during the course of the experiments. Nitrogen flow rate was adjusted with the GC's built-in rotameter. Data were collected on a

personal computer, equipped with a proprietary analog-to-digital converter, and proprietary software which recorded FID output voltage versus time. The raw data were stored as ASCII text files, for subsequent analysis.

B. Materials

Commercial-grade samples of a natural zeolite (Zeobrite M), and a modified zeolite product (Zeocarb Na), were obtained from Zeotech Corporation. Chemical analysis of these materials was also provided by Zeotech; the results are summarized in Table 2 (11). Zeolite samples were sieved with U. S. standard series sieves, and the -20 +40 mesh fraction was captured. The particle size distribution of the original samples was not evaluated, because these materials can be obtained in any desired size range. GC columns were assembled by packing measured amounts of zeolite in copper tubing. The columns were installed in the GC, and conditioned by heating at 250° C for at least eight hours, with nitrogen flowing through the column.

Analytical grade benzene and o-xylene, and commercial grade methane, were used in this study. Relevant properties of these compounds are summarized in Table 3 (12).

C. Methods

After conditioning a column, the GC oven temperature and carrier gas flow rate were adjusted to the desired conditions. Triplicate injections of 10 µL of methane gas were introduced, and the retention time (t_m) was measured. The retention time is defined as the centroid of the FID response versus time curve. One microliter aliquots of either liquid benzene or o-xylene were injected, and the FID output as a function of time was recorded. The corrected retention time of each compound was calculated as

$$t' = t_r - t_m$$

where t_r is the measured retention time of the aromatic compound, and t_m is the retention time of methane.

RESULTS

In the early stages of this research, 5 foot long, 1/8 inch columns were packed with -100 +120 mesh zeolite. These were installed in the GC oven and conditioned at 250° C. Within two hours of commencement of the conditioning, the flow of carrier gas through the column decreased from 42 to zero cm^3 per minute. This problem occurred with Zeobrite M. Subsequent columns were built with 1/4 inch tubing and -20 +40 mesh zeolite, to avoid this problem

Once the flow problem was solved, it was found that benzene could not be detected after injection on a 5 foot column packed with Zeobrite M, even using the GC's most sensitive attenuation setting. To solve this problem, two shorter columns were built, both 15 inches long. One was packed with Zeobrite M, the other with Zeocarb Na. The experimental conditions for both these columns were a temperature of 100° C, and a nitrogen flow rate of 40 cm^3 per minute.

The retention of methane on the Zeobrite M column is shown in Figure 2, and the retention of benzene is shown in Figure 3. The retention of methane on the Zeocarb Na column is shown in Figure 4, and the retention of benzene and o-xylene are shown in Figure 5. When reviewing these graphs, note the time scale used on the methane graphs is different than that of the benzene and o-xylene graphs. The corrected retention times, and elution velocities (v), for both columns are summarized in Table 4. The elution velocities were calculated by dividing the column length by the corrected retention time.

DISCUSSION

Considering the physical properties of benzene and o-xylene (Table 3), we see that these compounds are very volatile, and would expect them to elute relatively quickly from a 15 inch column. Instead, the corrected retention time is on the order of hours. We hypothesize that a molecular sieving effect caused the long retention times of benzene and o-xylene. Comparison of the sizes of these molecules (6.7 to 8.6 Å (13)) with the dimensions of the zeolite oxygen windows (4 to 7.2 Å) suggests this mechanism. However,

the retention mechanism will not be studied in detail in this research.

FUTURE RESEARCH

The length of time needed (as much as several hours) for elution of an aromatic compound from a 15 inch packed zeolite column is inconvenient from a research perspective. The next phase of research will be to construct shorter packed columns, to expedite the elution of organics from the zeolite. In addition to the Zeobrite and Zeocarb products, natural zeolites from several other U.S. producers will be evaluated. Those natural zeolites with the most promising retention characteristics will be impregnated with potassium permanganate. Columns packed with permanganate-impregnated zeolite will be constructed, and the removal of aromatic compounds will be measured and compared against removal by the unmodified zeolitic material. Retention and oxidation of other aromatic compounds, such as toluene and ethylbenzene will also be studied.

The proposed technology (i.e., use of permanganate-impregnated zeolites), offers the benefits of both adsorption and oxidation of the organic compounds. The zeolites are extremely inexpensive ($120 per ton) and resistant to extreme temperatures, acids and bases. The oxidant used (potassium permanganate) is also relatively inexpensive, and is known to oxidize many organic compounds. If successful, this technology could provide another alternative for the removal of organic compounds from gas streams.

ACKNOWLEDGMENTS

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REFERENCES

1 Hersh, C. K., *Molecular Sieves*, New York, Reinhold Publishing Corp., 1961.

2 Dyer, A., *An Introduction to Zeolite Molecular Sieves*, New York, John Wiley and Sons, 1988.

3 Eyde, T. H., and Shelton, V., "Zeolites," *Mining Engineering*, pp. 618-619, June 1991.

4 Eyde, T. H., "Zeolites," *Mining Engineering*, p. 44, June 1996.

5 Breck, D. W., *Zeolite Molecular Sieves; Structure, Chemistry, and Use*, New York, John Wiley and Sons, 1974.

6 Meier, W. M., and Olson, D. H., *Atlas of Zeolite Structure Types*, Zurich, Switzerland, International Zeolite Association, 1978.

7 Lee, D. G. *The Oxidation of Organic Compounds by Permanganate Ion and Hexavalent Chrome*, Open Court Publ. Co., La Salle, Illinois, 1980.

8 Fatiadi, A. J. , "The Classical Permanganate Ion: Still a Novel Oxidant in Organic Chemistry", *Journal of Synthetic Organic Chemistry* (2), pp. 85-206, 1987.

9 Klatte, F. U. S. Patent 5,278,112, January 11, 1994.

10 Klatte, F. personal communication with F. Cadena, March 27, 1996.

11 Husler, J., Analytical Report to Steve Peterson, Zeotech, Analytical Chemistry Laboratory, Dept. of Earth and Planetary Sciences, University of New Mexico, July 10, 1996.

12 Montgomery, J. H. and Welkom, L. M., Groundwater Chemicals Desk Reference, Chelsea MI, Lewis Publishers Inc., 1990.

13 Cadena, F., and Cazares, E., "Use of Organozeolites for the Removal of Organic Contaminants from Water", *in CMS Workshop Lectures, Vol. 8, Organic Pollutants in the Environment*, Boulder, CO, The Clay Minerals Society, 1996.

Table 1

Properties of Natural Zeolites

Zeolite	Dehydration Behavior	Typical Unit Cell	Oxygen Window	Window Size (Å)
Clinop-tilolite	Stable to 750° C	$Na_6Al_6Si_{30}O_{72} \cdot 24H_2O$	Eight-ring Ten-ring	4 x 5.5 4.1 x 4.7 4.4 x 7.2
Mordenite	Stable to 800° C	$Na_8Al_8Si_{40}O_{96} \cdot 24H_2O$	Eight-ring Twelve-ring	2.9 x 5.7 6.7 x 7.0

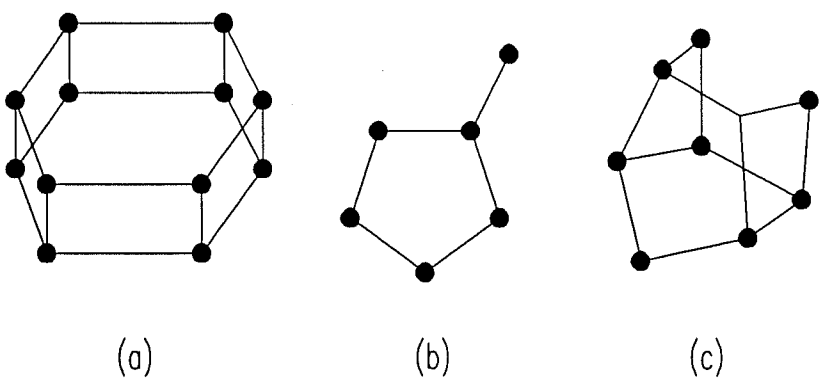

Figure 1 Secondary Building Units

(a) Double six ring (D6R) (b) complex 5-1 (c) complex 4-4-1

Table 2

Analysis of Zeolite Samples

Zeolite Name and Type	Zeobrite M Clinoptilolite/ Mordenite	Zeocarb Na Carbonized Clinop-tilolite
SiO_2	65.07	63.56
TiO_2	0.221	0.187
Al_2O_3	12.37	12.08
Fe_2O_3	0.79	0.73
FeO		
MnO	<0.001	0.036
MgO	0.355	0.59
CaO	1.58	2.42
Na_2O	3.70	2.60
K_2O	0.29	1.70
P_2O_5	0.026	0.022
H_2O (-)	4.1	2.7
H_2O (+) + CO_2	10.2	12.6
SO_4^{-2}	trace	0.5-1.0%
TOTAL	98.70	99.21

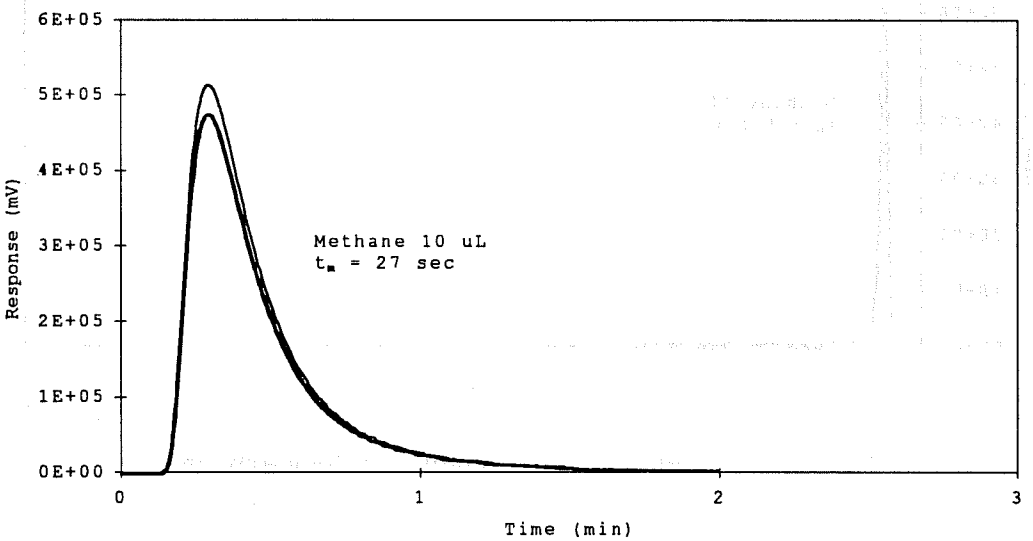

Figure 2 Retention of Methane on Zeobrite M

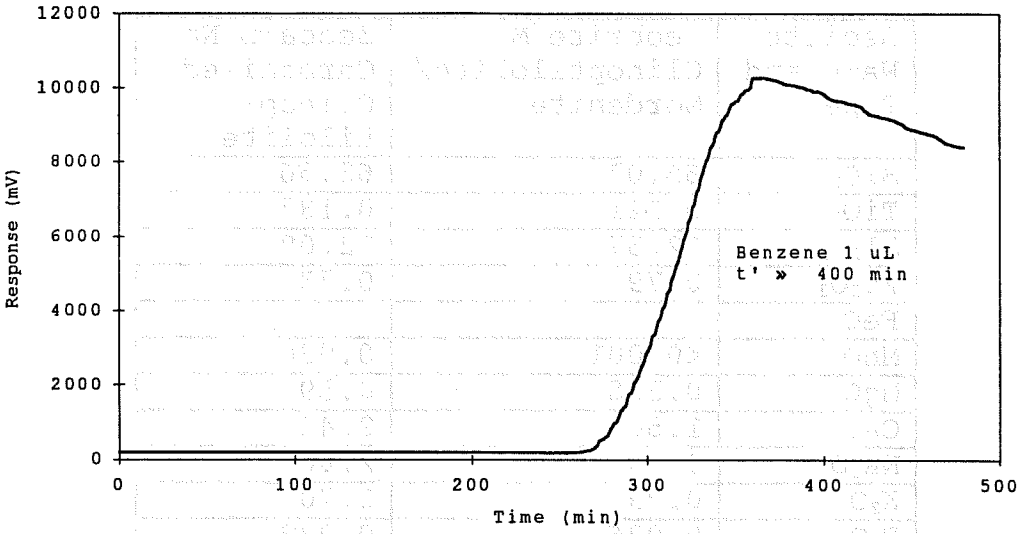

Figure 3 Retention of Benzene on Zeobrite M

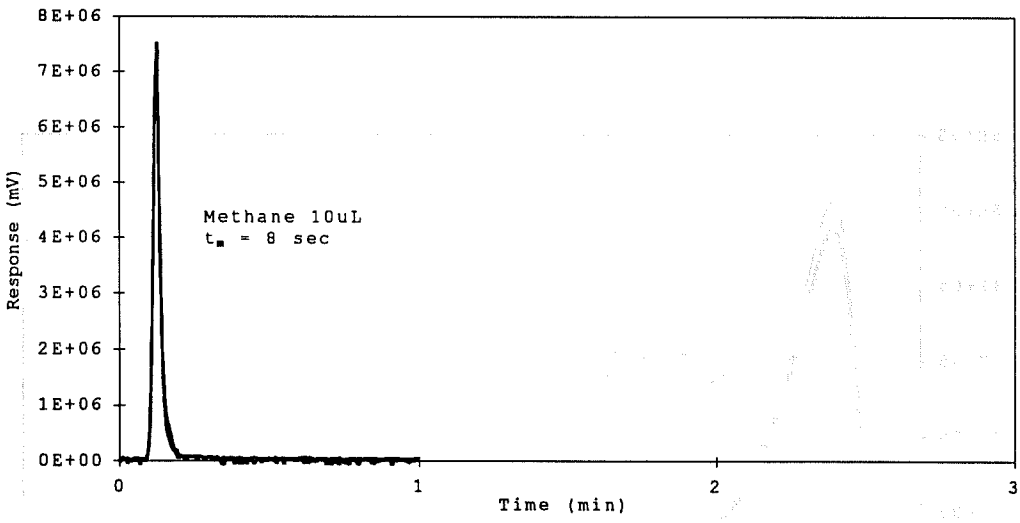

Figure 4 Retention of Methane on Zeocarb Na

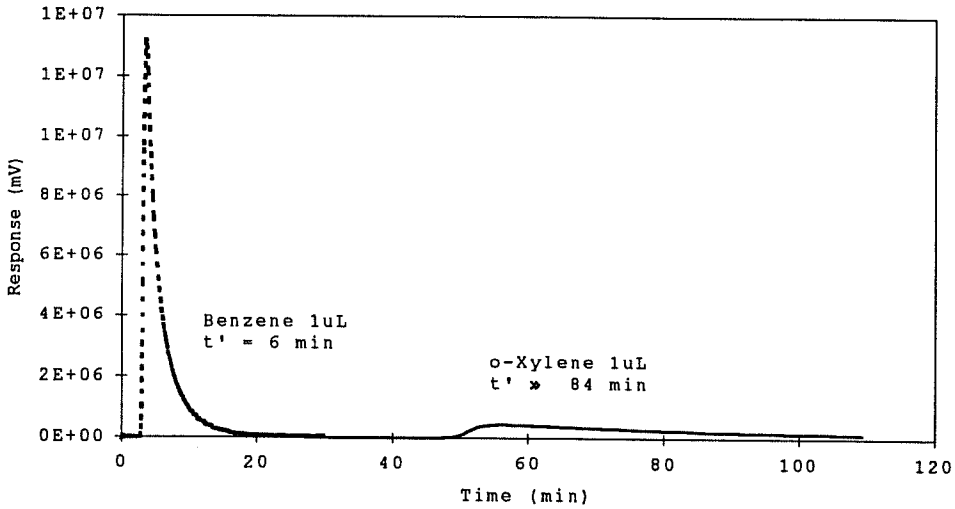

Figure 5 Retention of Benzene and o-Xylene on Zeocarb Na

Table 3

Properties of Aromatic Compounds (7)

Name	Boiling Point (°C)	Vapor Pressure (mm Hg at T° C)	Molecule Dimension (Å) ()
Benzene	80.1	76 mm at 20 1370 mm at 100.3 15200 mm at 221.5	6.7 x 7.4
o-Xylene	143-144	6.6 mm at 25 400 mm at 113.8	7.9 x 8.6

Table 4

Summary of Column Velocities

Column	Methane		Benzene		O-xylene	
	t_m (sec)	v (cm/min)	t' (min)	v (cm/min)	t' (min)	v (cm/min)
Zeobrite M	27	85	400	0.1	NA	NA
Zeocarb Na	8	286	6	6.4	84	0.5

Use of Photochemical Ozone Creation Potential in the Prioritization of Atmospheric Emissions from Petroleum Refineries

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ABSTRACT

The national ambient air quality standard for ozone is the most frequently exceeded standard in urban areas in the contiguous United States. Precursors of such tropospheric ozone concentrations include volatile organic chemicals (VOCs) and oxides of nitrogen. Control strategies for urban ozone typically treat VOCs as a single group of compounds without taking into account their different reactivities. Several studies have shown that the photochemical ozone creation potential (POCP) varies among classes of VOCs, with POCP being defined as the change in the amount of ozone formed due to a change in emission of that particular compound. Laboratory and photochemical trajectory modeling studies by others have been conducted, and POCP values for up to 75 organic compounds have been determined. Such POCP values vary with the class of compound, reaction times, and atmospheric temperatures. Therefore, urban ozone control strategies for stationary sources could be developed based on reducing the emissions of VOCs with the highest POCPs. This paper proposes reactivity-based VOC controls for stationary sources at petroleum refineries. For example, petroleum refineries emit nonmethane hydrocarbons (or VOCs) comprised of 80 to 90 percent alkanes; these saturated hydrocarbons have POCP values which are lower than for alkenes and alcohols. Nonmethane hydrocarbons released from refineries are prioritized herein based on their ozone production potential and their relative contribution to total VOC emissions. Such prioritization should be helpful in formulating petroleum refinery control measures to achieve higher tropospheric ozone concentration reductions with minimum emissions control requirements. This approach should be more cost-effective than across-the-board command and control approaches for all nonmethane hydrocarbon emissions from refineries.

INTRODUCTION

The current national ambient air quality standard (NAAQS) for tropospheric ozone is 0.12 ppm for 1-hour; and it is the most frequently exceeded standard in urban areas in the contiguous United States. Because of the human population exposed in urban areas and the magnitude of exceedances relative to both concentrations and hours per year, the Clean Air Act Amendments (CAAA) of 1990 designated five categories of ozone nonattainment areas and specified differential control requirements for state or urban area programs to facilitate reductions in ozone concentrations and ultimate attainment of the standard. As part of their normal 5-year review process for NAAQSs, the U.S. Environmental Protection Agency (EPA) is currently considering a modification in the ozone standard to between 0.07 to 0.09 ppm for an 8-hour period. However, of emphasis herein are the precursors of tropospheric ozone and their relative ozone production potential, and the implications of such relative to control strategies for atmospheric emissions from petroleum refineries.

Tropospheric ozone is formed as a result of photochemically-induced reactions of precursors such as volatile organic chemicals (VOCs) and oxides of nitrogen (NO_x). While there may be many subreactions, the overall atmospheric reaction can be simply expressed as:

$$VOCs + NO_x \xrightarrow{\nu} ozone$$

The term ν represents the sunlight-induced mechanism of ozone formation. Several factors can influence ozone production rates and subsequent concentrations; examples include the chemical reactivity of the VOCs (or hydrocarbons), atmospheric mixing, solar radiation intensity, and temperature. More specifically, the following factors have been identified as affecting tropospheric ozone concentrations at specific locations (1): the spatial and temporal distribution of emissions of VOCs and NO_x (both anthropogenic and biogenic); the composition (and reactivity) of the emitted VOCs; the spatial and temporal variations in the wind fields; the dynamics of the boundary layer, including stability and the level of mixing; the chemical reactions involving VOCs, NO_x, and other important species; the diurnal variation of solar insolation and temperature; the loss of ozone and ozone precursors by dry deposition; and the ambient background concentrations of VOCs and NO_x in, immediately upwind, and above the region of study.

RELATIVE REACTIVITIES OF VOCs

The fact that different organics have different abilities to produce ozone was recognized over 40 years ago (2). Various reactivity scales have been proposed to classify organic compounds such as nonmethane hydrocarbons based on their ability to produce ozone. Since such hydrocarbons initiate the production of organic radical species by reacting with hydroxy radicals, they can be classified with respect to their reactivity with hydroxy radicals, their rate of loss, their rate of ozone formation, and their incremental reactivity.

Implementation of a practical hydrocarbon reactivity scale was initiated as early as 1966 by the Los Angeles Air Pollution Control District. Their "Rule 66" limited solvent emissions on the basis of their capacity for promoting photochemical smog formation (3). Rule 66 was

aimed at controlling ozone formation by more severely limiting the emissions of highly reactive organics than emissions of lesser reactive organics. The emphasis was more on the nature of the emissions rather than on reducing the total quantity (4).

A second example of reactivity considerations in air quality management can be drawn from selected requirements for mobile sources as contained in the CAAA. Specifically, the emphases on using reformulated gasoline or other alternative fuels in urban areas characterized by more extensive ozone problems recognizes both the need to lower precursor emissions and modify their composition toward lower reactivity components.

Several laboratory and atmospheric modeling studies have focused on the photochemical ozone creation potential (POCP) of classes of VOCs, where the POCP is defined as the change in the amount of ozone formed due to a change in emission of that particular compound (5, 6, 7, and 8).

The percentage of various organics participating in photochemical reactions to form ozone was determined in an early laboratory study of 25 organic compounds to yield ozone. The percentage of the organic compound reacted after 6 hours of irradiation to yield ozone was determined. In general, it was found that only small percentages (5 to 15%) of alkanes participated in the reactions that lead to the production of ozone. Alkenes and aromatics were consumed to a greater extent, thus resulting in higher concentrations of produced ozone.

The individual involvement of various hydrocarbons in photochemical ozone formation has been studied by using the Harwell photochemical trajectory model. In 1987, this model was used for 37 hydrocarbons to determine the percentage of ozone production that could be attributed to each (6). In a 1991 study, which was more extensive than the 1987 study, the POCP was defined by subtracting the emissions of a particular hydrocarbon from a 69-component mixture and rerunning the photochemical model calculation (7). The difference in ozone concentrations between the base case and each of the 69 model experiments provided the measure of the contribution made by that individual compound. The POCPs of all 69 hydrocarbons were determined individually and also expressed relative to ethylene, where the absolute POCP of ethylene was determined to be 1.39 ppb ozone/ppb ethylene.

A 1992 study involved calculations for 75 organic compounds using a single-box trajectory model with meteorological and chemical conditions corresponding to summer high-pressure situations in southern Sweden (8). Calculations were made to simulate up to a 4-day period wherein ozone would be formed.

Table 1 summarizes the details of the POCPs of various alkanes, alkenes, and aromatics, and one alkyne, that are typically released from petroleum refineries as determined in the above-mentioned 1991 and 1992 studies (7 and 8). Additional information related to refinery emissions is in the next section. From Table 1 it can be noted that the POCPs are not available for all compounds from refineries. However, it can be observed that the POCPs for different hydrocarbons from the two studies are similar. These results can be used as one criterion in ranking hydrocarbon emissions from petroleum refineries. Additional information on atmospheric chemistry and lifetime considerations for each class of hydrocarbons is available elsewhere (9).

In summary relative to photochemical reactivities of organic compounds, although there are differences among various specific studies and proposed reactivity scales, the following general order of increasing reactivity has been consistently reported: alkanes have lesser reactivity than alkenes and alcohols.

HYDROCARBON EMISSIONS FROM PETROLEUM REFINERIES

Petroleum refineries have numerous potential sources that emit ozone precursors such as VOCs and NO_x. To determine the potential of refinery emissions to form ozone in the troposphere, it is necessary to consider the nature and concentrations of individual organic compounds, in addition to the total concentration of VOCs. However, due to analytical costs and time constraints, only a few studies have actually measured the concentrations of individual organic compounds from petroleum refineries (10, 11, 12, and 13). To serve as an illustration, Table 2 summarizes both background and refinery fenceline concentrations of various hydrocarbons at a Robinson, Illinois facility (12). The background concentrations were typically less than 10% of the fenceline concentrations of the compounds considered both as a group and individually. Further, if it is assumed that the fenceline concentrations are proportional to the emission inventory, it can be seen that alkanes (saturated hydrocarbons) represented about 88% of the total inventory, with aromatics at 8% and alkenes at 4% (12). The measurements were limited to selected alkanes, alkenes, and aromatics, and to acetylene. Higher alkanes and aldehydes were not measured; however, such emissions from refineries are not considered to be significant (14).

Individual stationary sources at refineries exhibit different emissions of organics; for example, Table 3 presents the percentages of different hydrocarbon groups emitted from various refinery processes (15). These emissions, which were related to an inventory in Los Angeles, were based on measurements of emission rates and the composition of the emissions from a statistically significant number of sources, and extrapolating the results to determine the total emissions. However, this data lacks detailed hydrocarbon speciations.

PRIORITIZATION OF REFINERY EMISSIONS OF NONMETHANE HYDROCARBONS

Nonmethane hydrocarbon (NMHC) emissions from petroleum refineries can be prioritized based on considering the relative proportions of such emissions, their respective POCPs, and the percentage of the emissions which might react within a specified period of time. For purposes of this example, the relative proportions of the emissions are assumed to be the same as the concentration readings at the fenceline from the Robinson, Illinois refinery study; both concentrations and relative proportions are shown in Table 2. Data on POCPs from two recent studies are shown in Table 1, with the key factor being the ppb of ozone produced per ppb of organic compound emitted. The reaction percentages are from the laboratory study referred to earlier (5). Based on these assumptions, the total ozone which might be produced was calculated using the following equations.

$$C_{mass} = 40.9(C_{ppm})(MW) \quad (1)$$

where

C_{mass} = mass concentration of nonmethane hydrocarbon (NMHC) resulting from the refinery ($\mu g/M^3$)

40.9 = numerical constant from ideal gas law for 1 atmosphere pressure and 25°C; also includes universal gas constant

C_{ppm} = volume concentration of NMHC (ppm)

MW = molecular weight of NMHC

Equation 1 is a typically used conversion equation to relate mass concentration and volume concentration. Since the final concentration of interest is ozone in ppb, Eq. 1 can be rewritten for the volume concentration of the precursor NMHC as:

$$C_{ppb} = 1000C_{ppm} \quad (2)$$

where

C_{ppb} = volume concentration of NMHC (ppb)

The ozone concentration prediction is then based on:

$$Ozone_{ppb} = (C_{ppb})(P)(POCP) \quad (3)$$

where

$Ozone_{ppb}$ = volume concentration of produced ozone from the NMHC (ppb)

P = NMHC reacted under irradiation for 6 hours to form ozone (fraction)

POCP = ratio of ozone produced per unit of NMHC (ppb ozone/ppb NMHC)

Combining equations 1,2, and 3 yields the following overall prediction equation:

$$Ozone_{ppb} = [\frac{C_{mass}\ (1000)}{(40.9)(MW)}](P)(POCP) \quad (4)$$

Tables 4 and 5 summarize the predicted ozone concentrations from equation 4 related to NMHC emissions from a refinery. The contribution of different classes of hydrocarbons to overall ozone production is summarized in Table 6. If the individual ozone concentrations shown in Tables 4 and 5 are summed, the maximum ozone concentration would be between about 36 and 41 ppb. Alkenes and aromatics together constitute

about 12% of total refinery VOC emissions; however, they produce about 55% of the total ozone; this distribution illustrate the importance of reactivity-based controls. Targeted control technologies with an increased focus on reducing alkenes and aromatics would yield more cost-effective results.

DISCUSSION OF RESULTS

The implication of the information in Tables 4 through 6 is that emissions control prioritization could be given to those NMHCs that would be anticipated to produce greater concentrations of tropospheric ozone. However, it should be recognized that the calculations summarized in Tables 4 to 6 were based on simplifying assumptions which should be further studied prior to detailed implementation of a prioritization program. The assumptions were focused on ozone production in local areas as opposed to the regional context, and the results are dependent upon other studies involving laboratory experimental data and theoretical calculations using a photochemical trajectory model. Further, the prioritization is based upon tropospheric ozone production and not on other considerations such as the potential health effects of the individual NMHCs.

There are other factors associated with tropospheric ozone formation that were not considered herein. One example is the ratio of VOCs to NO_x in urban air. Several recent studies have suggested that when the VOC/NO_x ratio is approximately 10 or less, the control strategy should be focused on reducing VOC emissions (16 and 17). This situation is termed VOC limiting. In contrast, in rural areas which might be characterized by ratios of 20 or more, some have suggested that VOC controls would be counterproductive in terms of the resultant ambient air quality. Further, specific factors such as atmospheric mixing and the intensity of solar radiation were not incorporated in the calculations presented herein.

Of potential growing importance is the current attention being given to regional approaches for ozone management. Such approaches have been implemented in the northeastern United States, and other regional studies are currently in progress. The prioritization of NMHC emissions from petroleum refineries as described herein does not address regional ozone concentrations nor long range transport of either the precursors or produced ozone.

If the prioritization scheme as described herein were to be incorporated within air quality management strategies for affected urban areas, several reporting and monitoring requirements would be necessary. First, more detailed regulations would be necessary to establish the program and to ensure adequate record keeping. Detailed inventories of the emissions of NMHCs would be necessary, with such details beyond the scope of the inventory requirements of current permitting programs. To develop such information would require detailed monitoring at refineries to establish appropriate emission factor information.

One possible benefit of the suggested prioritization scheme would be to encourage existing refineries to conduct internal control strategy planning. In this regard, early attention could be given to the application of control technologies for those stationary sources within refineries that emit NMHCs of higher reactivity. This approach should be more cost-effective than across-the-board command and control approaches

for all NMHC emissions from refineries. Regarding specific types of controls, technologies for the various classes of hydrocarbons described herein would involve applications of similar systems such as carbon adsorption or incineration.

Finally, several data needs and uncertainties should be considered relative to using POCPs for tropospheric ozone management in both urban and regional areas. Examples of such data needs and uncertainties include: there are many unknowns in the atmospheric chemistry of ozone; minimal systematic air quality data exists for ozone and precursors and other products, although an enhanced monitoring program has been recently implemented (18); there is a need for more specific emission inventories for VOCs from both natural sources and man-made sources; and more effective modeling of both urban area and regional ozone formation and transport is needed.

SUMMARY

This paper has addressed the consideration of the photochemical reactivities of organics emissions from petroleum refineries in the development of appropriate stationary source control strategies. It is recognized that the results are preliminary and subject to the stated assumptions. However, since air quality management efforts are becoming more complicated, it would seem appropriate, as well as in keeping with the CAAA of 1990, to focus attention on controlling emissions which reflect the greatest concerns regarding tropospheric ozone formation.

SELECTED REFERENCES

1. Cooper, C.D., and Alley, F.C., Air Pollution Control: A Design Approach, Second Edition, Waveland Press, Inc., Prospect Heights, Illinois, 1994, p. 587.

2. Haagen-Smit, A.J., et al., "Ozone Formation in Photochemical Oxidation of Organic Substances," Industrial and Engineering Chemistry, Vol. 45, No. 10, October, 1953, pp. 2086-2091.

3. Darnall, K.R., et al., "Reactivity Scale for Atmospheric Hydrocarbons Based on Reaction with Hydroxyl Radical," Environmental Science and Technology, Vol. 10, No. 7, July, 1976, pp. 692-696.

4. Dodge, M.C., "Combined Effects of Organic Reactivity and NMHC/NO_x Ratio on Photochemical Oxidant Formation: A Modeling Study," Atmospheric Environment, Vol. 18, No. 8, August, 1984, pp. 1657-1667.

5. Heuss, J.M., and Glasson, W.A., "Hydrocarbon Reactivity and Eye Irritation," Environmental Science and Technology, Vol. 2, No. 12, December, 1968, pp. 1109-1116.

6. Hough, A.M., and Derwent, R.G., "Computer Modeling Studies of the Distribution of Photochemical Ozone Production Between Different Hydrocarbons," Atmospheric Environment, Vol. 21, No. 9, September, 1987, pp. 2015-2033.

7. Derwent, R.G., and Jenkins, M.E., "Hydrocarbons and the Long Range Transport of Ozone and PAN Across Europe," Atmospheric Environment, Vol. 25A, No. 8, August, 1991, pp. 1661-1678.

8. Andersson-Skold, Y., Greenfelt, P., and Pleijel, K., "Photochemical Ozone Creation Potentials: A Study of Different Concepts," Journal of the Air and Waste Management Association, Vol. 42, No. 9, September, 1992, pp. 1152-1158.

9. Tallam, L.R., "Prioritization of Nonmethane Hydrocarbon (NMHC) Emissions from Petroleum Refineries Based on Photochemical Ozone Production Potential," M.S. Thesis, 1994, University of Oklahoma, Norman, Oklahoma.

10. Westberg, H.H., et al., "Ambient Hydrocarbon and Ozone Concentrations Near a Refinery - Lawrenceville, Illinois 1974," EPA-600/7-77-049, May, 1977, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

11. Sexton, K., and Westberg, H.H., "Photochemical Ozone Formation from Refineries," Atmospheric Environment, Vol. 17, No. 3, March, 1983, pp. 467-477.

12. Sexton, K., and Westberg, H.H., "Ambient Hydrocarbon and Ozone Concentrations Near a Refinery," EPA-600/3-025, April, 1983, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

13. Sexton, K., and Westberg, H.H., "Nonmethane Hydrocarbon Composition of Urban and Rural Atmospheres," Atmospheric Environment, Vol. 18, No. 6, June, 1984, pp. 1125-1132.

14. Veldt, C., Emissions of SO_x, NO_x, VOC, and CO from East European Countries," Atmospheric Environment, Vol. 25A, No. 12, December, 1991, pp. 2683-2701.

15. U.S. Environmental Protection Agency, "Utility of Reactive Criteria in Organic Emission Control Strategies: Application to the Los Angeles Atmosphere," EPA-600/3-76-091, August, 1976, Research Triangle Park, North Carolina.

16. Office of Technology Assessment, "Catching Our Breath -- Next Steps for Reducing Urban Ozone," OTA-0-412, July, 1989, U.S. Congress, Washington, D.C., pp. 3-26.

17. Wolff, G.T., "On a NO_x-focused Control Strategy to Reduce O_3," Journal of the Air and Waste Management Association, Vol. 43, No. 12, December, 1993, pp. 1593-1596.

18. U.S. Environmental Protection Agency, "EPA Promulgates Enhanced Ozone Monitoring Regulations," EPA 454/N-93-020, Vol. 3, No. 1, 1993, Washington, D.C.

Table 1: Absolute POCPs of Alkanes, Alkenes, and Aromatics (after 7 and 8)

Organic Compound	Absolute POCP of Compound (ppb/ppb)[a]	
	Ref. 7	Ref. 8
Alkanes		
Ethane	0.11 (1.3)[b]	0.14 (2.02)
Propane	0.58 (0.31)	0.67 (0.17)
i-Butane	0.44 (3.2)	0.49 (2.74)
n-Butane	0.58 (5.9)	0.59 (5.56)
i-Pentane	0.41 (3.4)	0.41 (9.55)
n-Pentane	0.57 (2.2)	0.16 (5.82)
Cyclopentane	n.a.[c]	n.a.
2,3-Dimethylbutane	0.53 (0.54)	
2-Methylpentane	0.73 (1.7)	0.63 (4.13)
3-Methylpentane	0.60 (1.2)	0.38 (2.92)
n-Hexane	0.59 (1.5)	0.51 (3.41)
Methylcyclopentane	n.a.	n.a.
2,4-Dimethylpentane	n.a.	n.a.
Cyclohexane	n.a.	n.a.
2,3-Dimethylpentane	n.a.	n.a.
3-Methylhexane	0.68 (0.57)	n.a.
2,2,3-Trimethylpentane	n.a.	n.a.
n-Heptane	0.74 (0.79)	0.92 (1.52)
Methylcyclohexane	n.a.	0.92 (1.34)
2,4-Dimethylhexane	n.a.	n.a.
2,3,4-Trimethylpentane	n.a.	n.a.
2,3-Dimethylhexane	n.a.	n.a.
2-Methylheptane	0.65 (2.0)	0.83 (0.20)
3-Ethylhexane	n.a.	n.a.
n-Octane	0.69 (0.58)	0.88 (0.03)
Ethylcyclohexane	n.a.	n.a.
Alkenes		
Ethylene	1.39 (2.3)	0.90 (4.34)
Propene	1.43 (0.83)	1.25 (1.89)
1-Butene	1.33 (0.52)	1.34 (0.34)
i-Butene	n.a.	n.a.
t2-Butene	n.a.	n.a.
c2-Butene	1.30 (0.72)	1.13 (0.09)
1-Pentene	n.a.	n.a.
t2-Pentene	n.a.	n.a.
c2-Pentene	n.a.	n.a.
Cyclopentene	n.a.	n.a.
Alkyne		
Acetylene	0.23 (1.3)	0.47 (3.83)
Aromatics		
Benzene	0.26 (1.7)	0.54 (2.23)
Toluene	0.78 (7.3)	0.76 (6.05)
Ethylbenzene	0.82 (1.4)	0.90 (0.86)
p&m-Xylene	1.31 (4.4)	1.02 (3.72)
Styrene	n.a.	n.a.
o-Xylene	0.93 (1.7)	0.73 (1.99)
i-Propylbenzene	0.79 (0.17)	0.86 (0.09)
n-Propylbenzene	0.68 (0.33)	0.73 (0.38)
1,3,5-Trimethylbenzene	1.59 (0.56)	1.17 (1.02)
1,2,4-Trimethylbenzene	1.67 (1.5)	1.17 (2.2)
1,2,3-Trimethylbenzene	1.63 (0.39)	1.21 (0.65)
p-Ethyltoluene	1.01 (0.63)	1.06 (0.66)
m-Ethyltoluene	1.10 (0.63)	1.07 (0.85)
o-Ethyltoluene	0.93 (0.51)	1.00 (0.40)
1,3-Diethylbenzene	n.a.	n.a.
1,4-Diethylbenzene	n.a.	n.a.

[a]ppb of ozone produced per ppb of compound
[b]Numbers in parentheses denote the percentages of the compounds used in the respective studies
[c]n.a. = not available

Table 2: Concentrations of Individual Hydrocarbons (in $\mu g/m^3$) in the Vicinity of a Petroleum Refinery (after 12)

Compound	Background		Fenceline	
Alkanes:	**46.68**	**(79.84)**[a]	**1088.10**	**(87.76)**
Ethane	5.54	(9.47)	51.46	(4.15)
Propane	11.25	(19.24)	212.20	(17.11)
i-Butane	2.35	(4.02)	60.46	(4.88)
n-Butane	8.77	(15.00)	222.73	(17.96)
i-Pentane	5.17	(8.84)	200.58	(16.18)
n-Pentane	3.93	(6.72)	88.88	(7.17)
2-Methylpentane	1.75	(2.99)	44.96	(3.63)
3-Methylpentane	1.06	(1.81)	25.54	(2.06)
n-Hexane	1.35	(2.31)	27.54	(2.22)
Methylcyclopentane	0.85	(1.45)	25.58	(2.06)
2,4-Dimethylpentane	0.46	(0.79)	9.54	(0.77)
Cyclohexane	0.42	(0.72)	9.81	(0.79)
2,3-Dimethylpentane	0.83	(1.42)	22.00	(1.77)
3-Methylhexane	0.48	(0.82)	11.61	(0.94)
2,2,3-Trimethylpentane	0.44	(0.75)	10.00	(0.81)
n-Heptane	0.60	(1.03)	15.58	(1.26)
Methylcyclohexane	0.48	(0.82)	14.77	(1.19)
2,4-Dimethylhexane	0.04	(0.07)	2.77	(0.22)
2,3,4-Trimethylpentane	0.00	(0.00)	2.33	(0.19)
2,3-Dimethylhexane	0.04	(0.07)	3.88	(0.31)
2-Methylheptane	0.27	(0.46)	8.69	(0.70)
3-Ethylhexane	0.23	(0.39)	8.50	(0.69)
n-Octane	0.35	(0.60)	8.69	(0.70)
Ethylcyclohexane	0.02	(0.03)	0.00	(0.00)
Alkyne:	**1.22**	**(2.09)**	**1.35**	**(0.11)**
Acetylene	1.22	(2.09)	1.35	(0.11)
Alkenes:	**4.10**	**(7.01)**	**48.74**	**(3.93)**
Ethylene	1.41	(2.41)	11.62	(0.94)
Propene	1.40	(2.39)	9.15	(0.74)
1-Butene	0.48	(0.82)	0.58	(0.05)
i-Butene	0.27	(0.46)	4.58	(0.37)
t2-Butene	0.17	(0.29)	3.65	(0.29)
c2-Butene	0.08	(0.14)	3.96	(0.32)
1-Pentene	0.25	(0.43)	5.08	(0.41)
t2-Pentene	0.02	(0.03)	2.38	(0.19)
c2-Pentene	0.02	(0.03)	6.12	(0.49)
Cyclopentene	0.00	(0.00)	1.62	(0.13)

Table 2: (continued)

Compound	Background		Fenceline	
Aromatics:	**6.47**	**(11.07)**	**101.73**	**(8.20)**
Benzene	1.10	(1.88)	9.65	(0.78)
Toluene	1.67	(2.86)	49.85	(4.02)
Ethylbenzene	0.45	(0.77)	5.54	(0.45)
p&m Xylene	0.88	(1.51)	12.77	(1.03)
Styrene	0.32	(0.55)	2.92	(0.24)
o-Xylene	0.59	(1.01)	6.31	(0.51)
i-Propylbenzene	0.04	(0.07)	0.81	(0.07)
n-Propylbenzene	0.23	(0.39)	1.50	(0.12)
p-Ethyltoluene	0.06	(0.10)	2.12	(0.17)
m-Ethyltoluene	0.04	(0.07)	1.35	(0.11)
o-Ethyltoluene	0.21	(0.36)	2.15	(0.17)
1,3,5-Trimethylbenzene	0.13	(0.22)	2.04	(0.16)
1,2,4-Trimethylbenzene	0.69	(1.18)	3.81	(0.31)
1,2,3-Trimethylbenzene	0.00	(0.00)	0.00	(0.00)
1,3-Diethylbenzene	0.06	(0.10)	0.00	(0.00)
1,4-Diethylbenzene	0.00	(0.00)	0.91	(0.07)

[a]Numbers in parentheses are the percentage of the total.

Table 3: Contribution of Organic Emissions from Refinery Sources (after 15)

Refinery Source	Percentage of Hydrocarbon Groups		
	Alkenes	Aromatics (excluding benzene)	Others (including alkanes)
Catalytic cracking	0.0	0.0	100.0
Separators and sewers	18.3	12.4	69.2
Pressure relief valves	11.9	11.9	76.2
Blowdowns	0.9	0.0	99.1
Vessel and tank maintenance	0.0	0.0	100.0
Cooling towers	15.0	10.2	74.8
Pump seals	12.1	8.9	77.3
Valves and flanges	15.1	11.1	73.8
Compressor exhaust	0.0	0.0	100.0
Compressor seals	18.1	5.6	76.3
Heater stacks	0.0	0.0	100.0
Others	6.5	9.4	84.7

Table 4: Production of Ozone from Alkanes Released from a Typical Petroleum Refinery

Hydrocarbon	Molecular weight	P (%)[a]	Predicted ozone production (ppb)[b]	
			After Ref. 7	After Ref. 8
Ethane	30	5	0.23	0.29
Propane	44	5	3.42	3.95
i-Butane	58	5	0.56	0.62
n-Butane	58	5	2.72	2.77
i-Pentane	72	15	4.19	4.19
n-Pentane	72	15	2.58	0.72
2-Methylpentane	86	15	1.40	1.21
3-Methylpentane	86	15	0.65	0.41
n-Hexane	86	15	0.69	0.60
Methylcyclopentane	84	15	-	-
2,4-Dimethylpentane	100	15	-	-
Cyclohexane	84	15	-	-
2,3-Dimethylpentane	100	15	-	-
3-Methylhexane	98	15	0.30	-
2,2,3-Trimethylpentane	114	15	-	-
n-Heptane	100	15	0.42	0.52
Methylcyclohexane	96	15	-	0.52
2,4-Dimethylhexane	112	15	-	-
2,3,4-Trimethylpentane	114	15	-	-
2,3-Dimethylhexane	112	15	-	-
3-Methylheptane	114	15	0.18	0.23
3-Ethylhexane	112	15	-	-
n-Octane	114	15	0.19	0.24
Ethylcyclohexane	110	15	-	-

[a]The percentage reacted factor was developed from data in reference 5; it was converted to a fraction for use in Equations 3 and 4.
[b]The original concentration for each listed hydrocarbon was from the fenceline concentration shown in Table 2. The POCP factor for each hydrocarbon was from Table 1.

Table 5: Production of Ozone from Acetylene, Alkenes, and Aromatics Released from a Typical Petroleum Refinery

Hydrocarbon	Molecular weight	P (%)[a]	Predicted ozone production (ppb)[b]	
			After Ref. 7	After Ref. 8
Acetylene	26	5	0.01	0.03
Ethylene	28	45	6.35	4.11
Propene	42	73	5.56	4.86
1-Butene	56	85	0.29	0.29
i-Butene	56	85	-	-
t2-Butene	56	85	-	-
c2-Butene	56	90	2.02	1.76
1-Pentene	70	90	-	-
t2-Pentene	70	90	-	-
c2-Pentene	70	90	-	-
Cyclopenetene	68	90	-	-
Benzene	78	13	0.10	0.21
Toluene	92	39	4.03	3.93
Ethylbenzene	108	29	0.30	0.33
p&m-Xylene	106	54	2.08	1.62
Styrene	104	*	-	-
o-Xylene	106	52	0.70	0.55
i-Propylbenzene	120	33	0.04	0.05
n-Propylbenzene	120	30	0.06	0.07
1,3,5-Trimethylbenzene	120	66	0.44	0.32
1,2,4-Trimethylbenzene	120	66	0.86	0.60
p-Ethyltoluene	120	52	0.23	0.24
m-Ethyltoluene	120	54	0.16	0.16
o-Ethyltoluene	120	52	0.21	0.23
1,3-Diethylbenzene	134	29	-	-
1,4-Diethylbenzene	134	29	-	-

*Not available.

[a]The percentage reacted factor was developed from data in reference 5; it was converted to a fraction for use in Equations 3 and 4.

[b]The original concentration for each listed hydrocarbon was from the fenceline concentration shown in Table 2. The POCP factor for each hydrocarbon was from Table 1.

Table 6: Contribution of Different Hydrocarbon Classes to the Maximum Ozone Production from a Typical Petroleum Refinery

Group	Percentage of Overall Emissions[a]	Predicted ozone production (ppb)	
		After Ref. 7	After Ref. 8
Alkanes	87.76	17.53 (42.8)[b]	16.27 (45.7)
Alkenes	3.93	14.22 (34.7)	11.02 (30.9)
Aromatics	8.20	9.21 (22.5)	8.31 (23.3)
Alkynes	0.11	0.01 (0.0)	0.03 (0.1)
Sum	100.00	40.97 (100.0)	35.63 (100.0)

[a]Percentages are from Table 2.
[b]Numbers in parentheses denote the percentages of total ozone production.

Table 6. Comparison of different Mycobacterium chelonae on the Medium Lame Fibobrution Zone a Typical Pabodiles Refinery

Group	Percentage of Overall Quality	Treatment group production (ppm)	
		After Ext. 1	After Ext. 2
Alfonso	80.06	10.56 (30.0)*	16.37 (26.7)
Alfonso	3.97	34.59 (30.1)	17.10 (30.0)
Amorwalle	1.99	0.83 (25.0)	5.73 (25.1)
Algrove	0.17	0.01 (0.0)	3.93 (7.3)
Sum	100.00	46.97 (100.0)	32.63 (100.0)

*percentages are from Table 3.
*Values in parenthesis denote the percentages of total zone production.

Nitrogen Cycling in Oil-Impacted Soils
II. Nitric Oxide Emissions

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Abstract:

A site in the Tallgrass Prairie Preserve (Nature Conservancy, Pawhuska, OK), accidentally contaminated with crude oil from a pipeline break, is being bioremediated using standard landfarming practices. As presented in the previous article (1), the site was divided into four sections to evaluate the role of nitrogen fertilization on bioremediation rate and microbial growth. Here, we focus on the observation that nitrogen fertilization results in extremely high levels of nitric oxide release from the remediation site. NO flux measurements indicated that urea fertilization induced a rapid, large increase in NO release (~700 ng $N/m^2 \cdot s$). For both ammonium sulfate and ammonium nitrate fertilization, significantly higher levels of NO release were observed over the unfertilized, contaminated soil. The NO flux, however, did not appear to correlate well with either net nitrification or denitrification metabolism. Interpretations of NO flux based on "leakage" from either nitrification or denitrification pathways are not sufficient to account for the large differences resulting from fertilization protocols.

Introduction:

Natural processes have a profound role in determining the composition and reactivity of our atmosphere. Recently, it has become clear that microbial processes in soil can act as a significant source for the photochemical oxidants NO and NO_2, collectively known as NO_x. Over the last ten years the estimated values for the production of NO_x from soil sources has increased; however, there is still a large degree of uncertainty and variability in the estimated total N flux. Overall, some estimates suggest that emissions from soil may account for as much as 40% of the global NO_x budget (2). The Southern Oxidants Study for the southern United States suggests a soil NO flux that contributes on the order of 19.1% for the total NO_x during the summer (3).

At present, most research has focused on the production of NO_x from either unperturbed grasslands or fertilized agricultural areas. A consensus of the available studies suggests that NO is the initial product which is released and that with either nitrogen fertilization, or with the clearing of vegetation, NO emissions increase (3). The NO flux levels have been highly variable and dependent on temperature and rainfall, but have generally ranged below 100 ng $N/m^2 \cdot s$ throughout the wide variety of grasslands and savanna/ chaparral areas that have been studied. Here we present our results showing nearly a 7 fold increase in NO flux from petroleum contaminated soils undergoing remediation.

Previous laboratory and field studies have supported a greater role for nitrification processes for NO production in soils (4). For this aerobic process, the NO flux is considered to result from the natural "leakage" during chemotrophic or heterotrophic ammonia oxidation, as opposed to a particular metabolic end-product. In a similar manner, both denitrification processes and abiotic reactions of nitrite at acidic pH have also been shown to produce NO from soil sources (3).

Two recent observations have provided evidence that NO production from bacterial sources may arise from processes that are not strictly obligatory nitrification or denitrification processes. First, the enzyme, nitric oxide synthase (NOS), has been reported in the common soil microbe Nocardia (5). Secondly, it has been reported that hemes systems can produce NO from several different oxygenated and hydroxylated amines independent of any terminal electron acceptor function (6).

Here, we present our data that indicates that the induction of naturally occurring microbial processes to enhance hydrocarbon degradation appear to enhance NO release. With the standard landfarming procedures as presented by Pope and Matthews (7) the petroleum contaminated site is diluted with clean soil (TPH of 3% or less), and bulking agents and fertilizer are added to enhance microbial growth and activity. The specific type of nitrogen fertilization appears to have large shifts in NO release.

Our study site involves the remediation of crude oil from a pipeline spill in the Tallgrass Prairie. The site (~80' x 80' x 1', 3% original hydrocarbon contamination) includes three contiguous sections fertilized at C:N ratios (100:3.3) with NH_4NO_3, $(NH_4)_2SO_4$, and urea. A control section received no added

chemical nitrogen fertilization. All the sections contained P_2O_5 and K_2O fertilization at C:P:K ratios of 100:1:1.

Chemical analyses of soil gases, nitrate, nitrite and ammonium levels and bacterial enumeration are as presented by our companion report (1). The predominant shift in soil microbial activity includes the induction of hydrocarbon degradation, ammonium oxidation and denitrification. Variable levels of microbial activity are observed for both nitrite and nitrite oxidation and denitrification processes. The role for this induction of hydrocarbon degradation capacity, nitrogen fertilization status and ion distribution suggests a complex variability with respect to the observed high level of NO emissions.

Material and Methods:

Site history, landfarming treatments, soil sampling, O_2/CO_2 gas surveys, bacterial enumeration and chemical analysis for NH_4, NO_3^-, and NO_2^- are as presented in Duncan et al. (1).

NO measurements were initiated two months after the start of remediation. This time period allows for the microbial populations to differentiate with respect to their various fertilization conditions. Each fertilized section was sampled over five different areas and averaged for the values reported.

The nitric oxide flux from the four remediation sections [NH_4NO_3, $(NH_4)_2SO_4$, urea and no nitrogen] was measured using a closed chamber method (8). A rectangular nalgene chamber (10" x 17 " x 10", L x W x H) was placed over the sampling section and inserted into a shallow groove dug into the soil. A 2' teflon hose inserted through the wall of the sampling chamber (2" above ground level) was connected to a Unisearch LMA3/LNC3 $NO/NO_2/NO_x$ monitoring system (Unisearch Inc., Toronto, Canada). This field portable instrument detects the chemiluminescence produced when luminol reacts with NO_2 in the presence of oxygen. NO is determined following the chromate-catalyzed conversion to NO_2. Previous publications have shown no interference due to NH_3 or other possible gaseous products expected in this field study (2). Temperature of the soil and air within the box were measured with a small thermocouple. In general, a slight lowering of air temperature was observed (~1-2 °C) over the total enclosure time. No significant shifts in soil temperature were observed so long as outside soil temperature remained below 27 °C, as was typically observed.

The flux of NO (or NO_2) is given by the sum of the measured flux (F_1) and the NO lost from the chamber to the atmosphere (F_2) due to dilutional effects.

$$F_1 = \frac{273}{T}\frac{V}{A}\frac{dc}{dt}$$

$$F_2 = \frac{(C_1 - C_o)\,Q}{22.4 * A}$$

where T is the absolute temperature of air in the chamber, V is the volume of the chamber, A is the enclosed soil area, *dc*/dt the rate of change of the NO concentration, C_o and C_1 are the concentrations of NO at times t_o and t_1 and Q is the pumping flow rate of the NO meter (1.5 L min^{-1}).

Sampling was initiated by first measuring ambient levels and then enclosing the box. NO was measured intermittently such that the pump was only on during a 10-20 second sampling time. In a typical determination, NO was measured at one minute intervals over the course of 10 to twenty minutes. For initial sampling, the NO flux in the urea fertilized section was greater than the maximal instrument detection limit (>200 ppb) and thus, NO flux calculations are an estimated lower limit.

Results and Discussion:

Ammonium, nitrate and nitrite levels:

At the initiation of NO sampling in July (two months into remediation treatment) all nitrogen fertilized plots showed relatively high levels of ammonium. NH_4^+ levels increased in the order from NH_4NO_3 (530 ppm) to urea (870 ppm) to $(NH_4)_2SO_4$ (950 ppm), as to be expected from the initial N loading. A constant increase in NH_4^+ was observed in the urea plot and is expected since there is a steady enzymatic hydrolysis of urea to produce ammonia and CO_2. At this time point in remediation, the soil from both the ammonium sulfate and ammonium nitrate fertilized sections were slightly acidic (~pH 6.5); however, the soil in the urea fertilized section was alkaline at pH=7.5, reflecting the net production of ammonia and CO_2.

Evaluating the net nitrogen flux is difficult since all three species, NH_4^+, NO_3^-, and NO_2^-, can be lost through leaching and, for NH_3 and NO_2^-, through evaporative, abiotic processes. Nevertheless, estimates of the net NO_3^- production levels showed roughly similar rates regardless of the fertilization protocol.

As expected, nitrate levels were highest in the ammonium nitrate fertilized section. After an early rapid loss, the concentrations of oxidized nitrogen in the ammonium nitrate fertilized plot was relatively constant over time. As an estimate of production based on the slight increase in nitrate observed during the second month, approximately 11% of the total ammonium in the ammonium nitrate fertilized section could have been oxidized. Based on total ammonium loss from the start of remediation, a maximum of 22% of ammonium could have been converted to nitrate. Using the average of these values, approximately 16% of the ammonia could be considered to be oxidized to nitrate over the initial two month period.

The ammonium sulfate plot showed a similar, but 125 ppm lower level of nitrate formation after two months. The overall level of nitrate; however, was still increasing. Nevertheless, the calculated NO_3^- production rate was similar. Based on either nitrate increases or ammonium losses, approximately 15% of the

originally added ammonia had been converted at two months. Thus, in summary, for both ammonium nitrate or ammonium sulfate, conversion of ammonium to nitrate was on the order of 15% of the originally added total ammonia.

In contrast to these results, the urea fertilized plot showed less nitrate (only 90 ppm corresponding to 6% net nitrification) but had an extremely high level of nitrite (130 ppm). Only very minor trace amounts (< 4 ppm) were ever observed in the other sections. The urea plot nitrite level would correspond to approximately 10% of the total nitrogen being oxidized to nitrite. Overall, then, the urea fertilized section thus shows a total level of 16% ammonium oxidation, similar to the other sections, but without complete oxidation.

Correlation of NO flux:

Measurement of NO flux using the enclosed chamber method typically showed rises in NO as shown in Figure 1. This figure shows the rapid rise to 120 ppb NO observed over one site on the ammonium sulfate fertilized section during the second month of remediation. Variability was rather large throughout all sites, but initially, only the urea sites had high concentrations of NO in excess of 200 ppb. For the Unisearch instrument used in this study, 200 ppb is the detection limit of the instrument, and thus, NO flux may be underestimated at these high flux levels.

At the initial measurement time two months following the start of remediation, NO flux increased from control prairie with minimal NO flux (or even uptake), to the control (no nitrogen) remediation site with flux levels of less than 20 ng $N/m^2 \cdot s$ (Figure 2). The flux jumped over three fold upon fertilization with either ammonia or nitrate, with the levels of NO flux ranging below 100 ng $N/m^2 \cdot s$ for either fertilization protocols. In contrast, the urea fertilized section had fluxes averaging at least 650 ng $N/m^2 \cdot s$ (Figure 2). As mentioned above, the urea fertilized plots had such an excess of NO that it exceeded the detection limit of the luminol analyzer at 200 ppb within 1 minute of measurement.

Within the third month of remediation, NO flux continued to be extremely high within the urea fertilized area. However, the flux also increased in the ammonium sulfate fertilized section. During this time there was not any drastic shift in nitrate, nitrite or ammonium levels. Although high levels of nitrite were observed in the urea plot, at no time did the level of nitrite in the ammonium sulfate fertilized plot increase beyond 3ppm.

Based on the total N that was initially added and converted to oxidized nitrate or nitrite, the NO flux in the urea fertilized section would correspond to over 3.3%. At present, it appears as if the ammonium sulfate plot is also approaching this value. Considering the similar levels for ammonia, it is difficult to explain the large differences in NO flux based on autotrophic ammonium oxidation.

Although the urea section did exhibit a high level of nitrite, no such concomitant increase in nitrite levels has been observed during the increase in NO flux in the other sections. Very low numbers of nitrite oxidizers were found in all

plots prior to the second month of sampling, and overall, increased in all but the urea plots into the third month. Thus, inhibition of autotrophic nitrification is consistent with the microbial data and nitrite levels in the urea plot, but is not consistent with the lack of buildup of nitrite with ammonium sulfate or with the increasing level of NO flux in either ammonium sulfate or ammonium nitrate plots. Overall, the lack of nitrite oxidizers does not appear to be a viable explanation for the flux difference. As for anaerobic processes, all plots had similar levels of denitrifiers and therefore, differential denitrification seems unlikely as a major source for the large differences between the plots.

Overall, it appears that the net ammonium oxidation, either autotrophic or heterotrophic, cannot by itself be used to predict net NO flux. The classical concept of "leakage" from nitrification pathways may appear capable of explaining the observed differences in NO flux at least for the urea plot, but other factors appear to play a role. It appears that assimilatory processes only indirectly leading to net nitrification may be of importance. Two such processes are the induction of NOS-containing microbes and/or the induction of a family of oxidases capable of generating NO. Of these two possibilities, MPN analysis of the different fertilized sections has not shown any clear differences in the number of microbes capable of hydrocarbon oxidation capacity, ammonium oxidation or denitrification levels, but the general classifications may miss significant shifts in species composition. Minor pH shifts observed at the beginning of remediation in the urea plot may have facilitated the growth and/or inhibition of nitrite oxidizers. The role for autotrophic versus heterotrophic nitrification and the shifts in the particular species composition are presently under further investigation.

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References:

1. Kathleen Duncan, Eleanor Jennings, Kelly Burnette, Susan Hettenbach, Ganesh Subramaniam, Ramesh Narasimhan, Arati Kolhatkar, Karen Durham, Robert Ingraham, Vu Song Huy Le, Oanh Nguyen, Marlycia Shoulders, William Potter and Kerry Sublette. "Nitrogen Cycling in Oil Impacted Soils: I. Microbial Effects". Proceedings of the Third International Petroleum Conference, Pennwell Press, Tulsa, OK. *In Press*.

2. Williams E. J., Hutchinson G. L. and F. C. Fehsenfeld. "NO_x and N_2O emissions from soil", *Global Biogeochemical Cycles*, 6, 351-388, 1992.

3. Chameides W. L. and Ellis B. Cowling. "*The State of the Southern Oxidants Study: Policy Relevant Findings in Ozone Pollution Research*", 1988-1994.

4. R. Lal, John Kimble, Ellisa Levine and B. A. Stewart. "Soils and Global Change", *Advances in Soil Science*, Chapter 18, 219-236, 1995.
5. Yijun Chen and John P. N. Rosazza. "Purification and Characterization of Nitric Oxide Synthase from a Nocardia Species", *J.Bacteriol*, 177, 5122-5128, 1995.
6. Mansuy D, J. L. Boucher and B. Clement. "On the Mechanism of Nitric Oxide Formation upon Oxidative Cleavage of C=N(OH) bonds by NO-Synthases and Cytochromes P450", *Biochimie*, 77, 661-667, 1995.
7. Pope D. F. and J. E. Matthews. *Bioremediation Using the Land Treatment Concept*. EPA/600/R-93/164, Robert Kerr Environmental Research Laboratory, Ada OK, August 1993.
8) Ralph J. Valente and Frank C. Thornton. Emissions of NO From Soil at a Rural Site in Central Tennessee, *J. Geophysical Res.*, 98, 16745-16753, 1993.

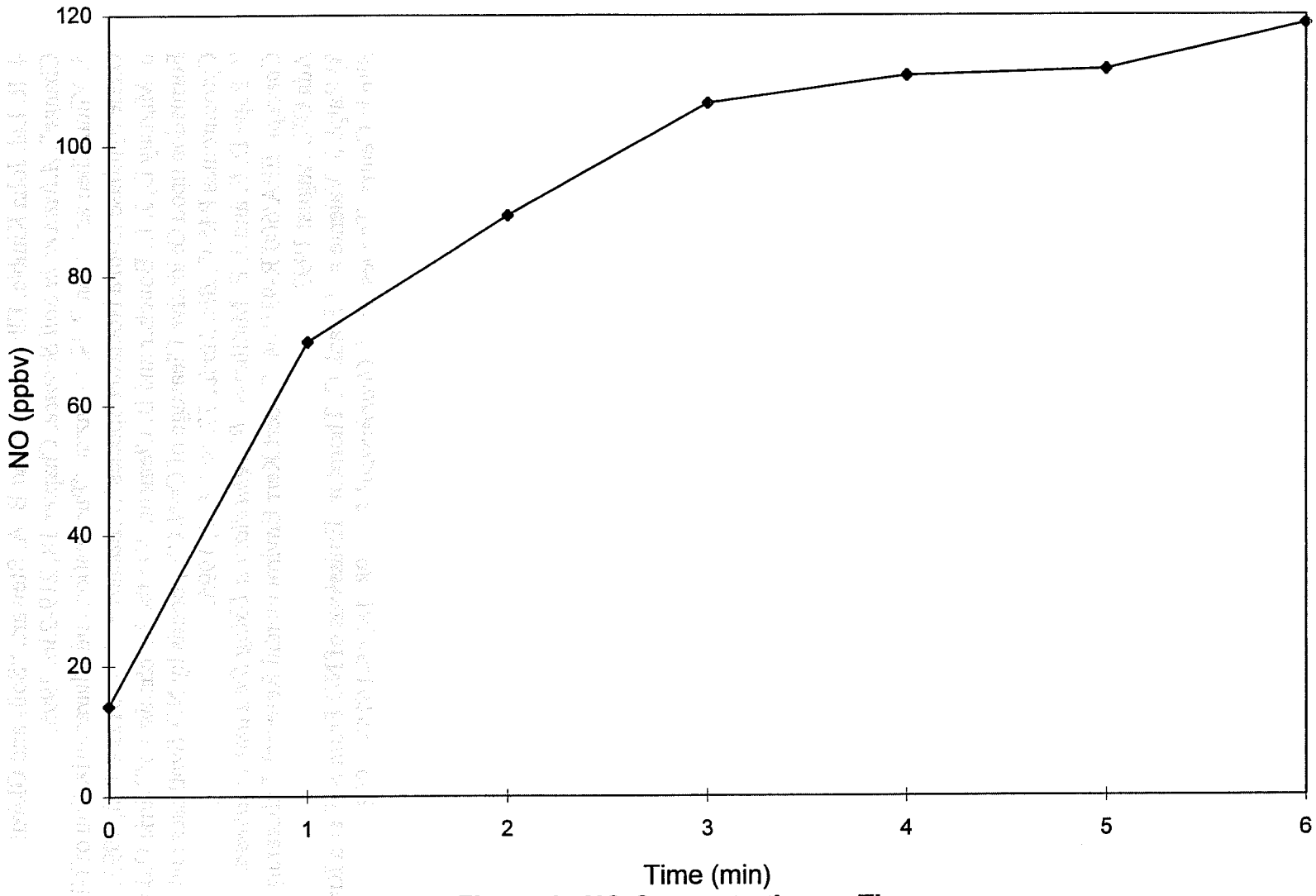

Figure 1. NO Concentration vs Time
Closed Chamber Method

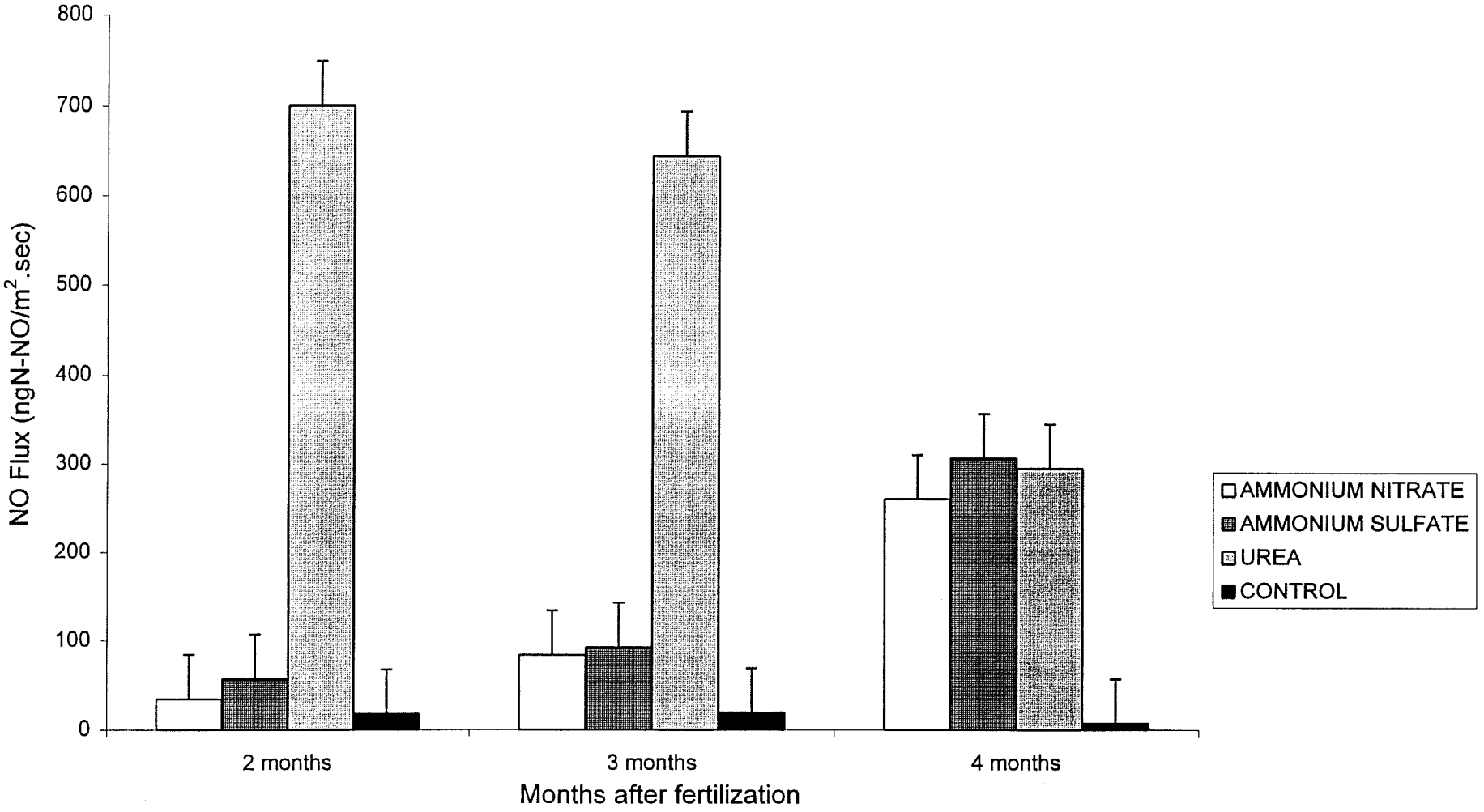

Figure 2. NO Flux for Tallgrass Prairie

Formaldehyde Emissions from Natural Gas-Fired Internal Combustion Engines

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Abstract

Until recent years, there was little information available on emissions of hazardous air pollutants (HAPs) from natural gas industry sources. However, due to regulatory requirements set forth in Title III of the 1990 Clean Air Act Amendments (CAAA) and other state regulations, emissions of toxic air pollutants have been studied in more detail.

Natural gas-fired internal combustion (IC) engines used for compression and transmission are HAP sources. Under the CAAA Title III, Maximum Available Control Technology (MACT) will be established for IC engines by the year 2000. Since formaldehyde is the only HAP present in engine exhausts at high enough levels to potentially exceed EPA's 10 ton per year "major source" threshold, formaldehyde emissions could have a significant impact on the environmental requirements of natural gas plants.

As part of the Gas Research Institute's (GRI) effort to facilitate industry participation in EPA's MACT development, measurements from internal combustion engines were taken to expand the industry's information base. GRI's test results are the basis for emission factors used in the revised "HAPCalc" program to be released in October 1996. Although more information is needed to gain better understanding of formaldehyde emissions from IC engines, factors which are believed to influence these emissions will be discussed. Since the method used to estimate formaldehyde emissions may significantly impact the results, an EPA valid method for testing formaldehyde from IC engine exhaust has been established. Other factors influencing emissions of formaldehyde include engine design, size and age; operating conditions; maintenance routines and schedules; and emission controls.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has classified formaldehyde as a probable human carcinogen, and it is one of 189 HAPs hazardous air pollutants (HAPs) listed under Title III of the Clean Air Act Amendments (CAAA). It is also of particular interest due to its photochemical reactivity in ozone formation. As a result, formaldehyde emissions from natural gas fired internal combustion (IC) engines must be considered when evaluating the environmental requirements of natural gas transmission, storage, and processing facilities. Engines in the natural gas industry are used primarily to power compressors used for pipeline transportation, field gathering, i.e., collecting gas from wells, underground storage, and gas processing plant applications, i.e., prime movers. (1) The quantity of formaldehyde emissions will depend on the number of engines, design type, operating conditions and maintenance procedures at a facility.

This paper provides a summary of available information which consists primarily of recent data collected from studies funded by the Gas Research Institute (GRI). A brief review of regulatory considerations and requirements is provided, followed by a review and comparison of the various methods of estimating formaldehyde emissions from IC gas engines. The method used to estimate formaldehyde emissions may significantly impact the results, which is demonstrated through an example of a small gas processing plant whose engine emissions are estimated using four different calculation methods.

Formaldehyde formation and destruction pathways are also described, to aid in understanding the factors which influence emissions. Based on GRI's research, formaldehyde emissions are influenced by engine design, operating conditions, controls, and maintenance routines and schedules. This reseach has provided a better understanding of formaldehyde emissions from IC engines, however, more information is needed to prepare for regulatory development activities.

REGULATORY CONSIDERATIONS

The 1990 Clean Air Act Amendments (CAAA) establishes a regulatory program to reduce emissions of air toxics. Formaldehyde is one of the 189 pollutants designated as a HAP under Title III of the CAAA.

It is the only HAP present in natural gas-fired IC engine exhausts at high enough levels to potentially exceed EPA's "major source" threshold.[1] Formaldehyde emissions from any single engine are not significant, however, total horsepower at a facility may have an impact.

Several important regulations applicable to HAP sources depend on the designation of the facility as "major." For example, a major HAP source must meet EPA's Maximum Available Control Technology (MACT) standards which are being developed for each industry source category. These regulations could have large economic and operational impacts on the gas industry. MACT requirements for the oil and gas production industry are targeted for November 15, 1997, and specific requirements for the stationary IC engine category are scheduled to be released by the year 2000.(2) Engine test data and other information resulting from the GRI sponsored research, may be used to establish baseline emission levels for potential control strategies, and may facilitate industry participation in EPA's MACT based regulation development.

"Major" gas industry sources must also meet requirements of Title V Operating Permit regulations. A Title V permit must list all applicable air quality-related requirements and propose a test method for each pollutant. Additional requirements include reporting test method results, and submitting a compliance certification annually.

In some instances, a facility which is otherwise not considered "major," e.g., for the criteria pollutants NOx or CO, may be considered "major" for formaldehyde. This is due to the (order of magnitude) lower threshold limit for HAPs.[2] Based on the latest emission factors developed by GRI, the highest formaldehyde emission rates (0.23 g/hp-hr) were found in 4-stroke clean-burn engines. A gas plant with 5000 total site horsepower, operating 4-cycle clean-burn engines, would be a major source solely due to its formaldehyde emissions.

Generally, the lowest formaldehyde emission rates (0.04 g/hp-hr) were found in 4-stroke lean-burn direct injected engines. For these engines, 25,900 site horsepower would be required to reach the 10 tpy major source level. (3)

State regulations must also be considered when evaluating formaldehyde emissions. Several states such as California, Texas, Louisiana, Colorado, New Mexico, and Kentucky, have air toxics programs in place or in the developmental

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[1] Facilities which emit 10 tons per year (tpy) of any single HAP or 25 tons per year of any combination of HAPs are considered to be "major" sources. In the case of formaldehyde emissions from gas-fired engines, only the 10 tpy threshold level is a concern as other HAP emissions are very low or negligible.

[2] The "major" source threshold level for criteria pollutants is 100 tpy versus only 10 tpy for HAPs such as formaldehyde.

phase that may effect the gas industry. State programs must be at least as stringent as federal regulations but in some cases may be more stringent.

METHODS FOR ESTIMATING HCHO EMISSIONS

In lieu of measuring formaldehyde emissions from engines, factors derived from test data may be used to estimate typical emissions. There are several sources of emission factors for natural gas fired IC engines. These sources include EPA's Compilation of Air Pollutant Emission Factors (AP-42) and Air Emissions Species Manual Volume I; GRI's HAPCalc software program Version 1.0; GRI's latest report titled "Measurement of Air Toxic Emissions from Natural Gas-Fired IC Engines at Natural Gas Transmission and Storage Facilities;" and a soon-to-be-released GRI HAPCalc Version 2.0 program. These sources and associated test methods are summarized in Table 1.

Fourier Transform Infrared (FTIR) Spectrometry Test Method

Until recently, there were no EPA-validated sampling and analytical methods for measuring formaldehyde and other aldehydes from natural gas-fired internal combustion engines. As part of GRI's research program to develop engine emissions measurement data, GRI conducted a study for validating the extractive Fourier Transform Infrared (FTIR) spectroscopy method.[3] The results of this validation testing were approved by EPA in July 1995.[4] The validation testing also included measurements of NOx, CO, CO_2, and moisture in engine exhaust. Therefore, the FTIR test protocol serves as a single measurement approach with which the industry can monitor air toxics and criteria pollutant emissions from engines simultaneously.[5] (4)

The FTIR approach provides for collection of an entire IR spectrum in a few seconds allowing selection of analysis regions. FTIR equipment includes a

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[3] The engine test data was validated according to EPA Method 301, "Field Validation of Pollutant Measurement Methods from Various Waste Media." Method 301 is not a measurement method but is a set of procedures to be followed in validating a proposed test method for a particular emission source or source category.

[4] EPA indicated that the test results "can be considered valid according to Method 301 for this source and similar sources" and the draft FTIR test protocol based on the validation testing results "may be used at any gas-fired facility.

[5] Since EPA reference test methods exist for measuring NOx, CO, CO_2, and moisture (Method 7E, 19, 3A, and 4, respectively), a paired sampling system was employed. Field measurements were based on a slip stream of the IC engine exhaust through a heated transfer line and delivery of a portion of this sample stream to the analytical instruments for concentration measurements. FTIR analysis of this extracted sample was performed on a hot/wet basis, as removal of moisture can result in losses of aldehydes. (4)

standard interferometer, associated optical support, and a computer system. In this method, the flue gas is continuously extracted from the engine and a portion of the gas is conveyed to the FTIR analytical components. An infrared spectrum of the flue gas is obtained by passing an infrared beam through the gas sample contained in a gas cell. Identification and quantification are performed by comparing sample spectra to reference spectra of compounds. No laboratory costs are involved because the results are obtained immediately during the test. (5)(6)

Manual Test Methods: CARB Method 430, and SW-846 Method 011

The two most common manual test methods, i.e., California Air Resources Bureau (CARB) Method 430, and SW-846 Method 011, are based on collecting emission samples in dinitrophenylhydrazine (DNPH). The formaldehyde present in the sample reacts with the DNPH to form formaldehyde-dinitrophenylhydrazone derivatives. The derivatives are extracted and analyzed by high performance liquid chromatography.(5)

GRI has found FTIR spectroscopy to be more accurate than either of the manual test methods. In several instances aldehydes were measured above detection limits using FTIR, but not detected at all in the analyses of the same samples using the manual methods.[6] It is believed that nitrogen dioxide (NO_2) in engine exhaust interferes with the DNPH measurement method.(4) Furthermore, test results varied depending on how much NOx was present in the sample.(7)

Other Test Methods

Several other test methods referred to in the literature, include the use of a spectrophotometer, or a mass spectrometer. In the spectrophotometric method, formaldehyde in the sample reacts with parasoaniline and sodium sulfite, forming a purple chromophore. The intensity of the color is measured spectrophotometrically and gives a precise measure of formaldehyde concentration in the sample. This method may have the same interference problems as CARB Method 430 or Method 0011, discussed above.(6) Mass spectrometry is used to identify species based on mass and characteristic patterns resulting from ion decomposition reactions. Gaseous molecules are ionized through exposure to an electron beam and are separated by mass. Most compounds have distinctive resulting mass spectra.(5)

[6] In several of these cases, trace amounts of aldehydes were found in the field blanks. Impinger solutions were observed to be clear instead of the orange color typically associated with DNPH, indicating potential cross-reactions that consumed the reagent. (4)

Comparison Of Test Methods And Estimation Methods

GRI HAPCalc Version 1.0 contains formaldehyde emission factors for natural gas IC engines. These factors were based on a comprehensive review of published emissions test information, including past GRI programs; EPA databases used to develop AP-42 factors; information from state agencies; and confidential GRI member-company test data. Altogether, data from 40 engines was utilized in developing the composite formaldehyde emission factors in HAPCalc 1.0. Most of the engines were tested using the manual CARB Method 430; thus, the data provided in HAPCalc 1.0 is suspect due to the test inaccuracies discussed above.

Other sources of formaldehyde emission factors for natural gas-fired IC engines include EPA's AP-42 which contains data for only 2-stroke lean burn engines and 4-stroke rich burn engines (1); and EPA's "Air Emissions Species Manual" which contains limited data from only two engines utilizing ionization detection gas chromatography (FID/PID GC).(9)

The most recent source of published formaldehyde emission factors for gas-fired engines is GRI's February 1996 report titled, "Measurement of Air Toxic Emissions from Natural Gas-Fired Internal Combustion Engines at Natural Gas Transmission and Storage Faciities." This report contains average emission factors from 16 engines (13 models) and several testing campaigns using the FTIR test method described above. Information on the engines tested is provided in Table 2.

GRI is expected to release HAPCalc Version 2.0 in October 1996. This program will include average emission factors for criteria pollutants and HAPs derived from FTIR test data. Users will also have the option of using factors from AP-42 or from the previous HAPCalc Version 1.0. The objective is to provide options to use emission factors which are best suited to specific engines. Options will also be provided in the program to include specific engine parameters such as make and design, modifications and/or controls, and horsepower rating.(10) HAPCalc Version 2.0 will contain data for engines which burn non-pipeline quality gas as well.(8)

Example: Formaldehyde Emissions From Six Gas-Fired IC Engines

For comparison purposes, formaldehyde emissions from 6 uncontrolled natural gas fired IC engines ranging from 1650 hp to 2500 hp were estimated using the available methods described above. Two 4-cycle rich-burn and four 2-cycle lean-burn engines operating 8760 hours per year were compared as this is the only comparison that can be made between GRI and AP-42 formaldehyde emission factors. The results, summarized in Table 3, indicate that AP-42 yields the highest formaldehyde and total HAP emissions. The next highest emissions

are derived from GRI test data, followed by HAPCalc 1.0, and the EPA Air Emissions Species Manual.

Estimated emissions may vary widely depending on the engine design and emission factors used. For example, for the 2-stroke lean burn family, the AP-42 factor is approximately one order of magnitude higher than the GRI test data. The opposite is true for the 4-stroke rich burn emission factors. Table 4 provides a summary and comparison of formaldehyde emission factors for each engine type.(3)

Formaldehyde Emissions -Correlation to THC and CO emissions

It is possible to use either total hydrocarbon (THC) or carbon monoxide as an indicator of formaldehyde emissions. To accomplish this, each engine type must be tested under different conditions to form a database of emission rates of formaldehyde and CO and/or THC under these specific conditions. From the baseline correlation developed for each engine type at a facility, it is possible to predict the formaldehyde emission rate when the THC or CO emission rate is known. (6)

Table 1

METHODS FOR ESTIMATING FORMALDEHYDE EMISSIONS FROM NATURAL GAS-FIRED IC ENGINES

	SOURCE &/OR TEST METHOD	NO. OF ENGINES
EPA AP-42	METHOD 430 (CARB); 0011 MASS SPECTOMETER	N.A.
EPA AIR EMISSIONS SPECIES MANUAL	FID/PID GC MBTH METHOD	2
HAPCalc VERSION 1.0 (GRI)	EPA AP-42 (CARB 430; 0011; Mass Spec.)	40
	OTHER PUBLISHED DATA	
	MEMBER TEST DATA	
GRI LATEST RESEARCH	FTIR METHOD	16
HAPCalc VERSION 2.O (GRI)	FTIR TEST DATA	16
	AP-42 (CARB 430; 0011; Mass Spec.)	N.A.
	HAPCalc VERSION 1.0	40

Table 2

ENGINES TESTED USING FTIR

Cooper Bessemer; Ingersoll-Rand; Clark; and Waukesha: 1000 Hp To 5000 Hp Using Pipeline Quality Gas

Points	#Engine Models	No. Of Engines	No. Of Data
2-STROKE LEAN BURN	5	6	21
2-STROKE CLEAN-BURN	3	3	10
4-STROKE RICH BURN	2	3	8
4-STROKE LEAN BURN	2	3	9
4-STROKE CLEAN BURN	1	1	9
TOTAL	13	16	58

Table 3

CALCULATED HAP EMISSIONS FROM SIX GAS-FIRED IC ENGINES

	TOTAL HAPS		FORMALDEHYDE	
	LBS/HR	TONS/YR	LBS/HR	TONS/YR
EPA SPECIES MANUAL	0.74	3.23	0.4	1.73
GRI HAPCalc VERSION 1.0	2.74	12.00	2.35	10.29
GRI TEST DATA (FTIR)	4.92	21.57	4.58	20.06
EPA AP-42	27.71	121.35	27.56	120.70

Table 4

HCHO EMISSION FACTOR COMPARISON

	g/hp-hr		
	GRI Test data	GRI Literature	EPA AP-42
2-Stroke Lean-Burn	0.18	.088	1.3
2-Stroke Clean-Burn	0.16	na	na
4-Stroke Rich-Burn	0.10	0.062	.0072
4-Stroke Lean-Burn			
Direct Injected	0.040	0.10	na
Port Injected	0.14	0.10	na
4-Stroke Clean Burn	0.23	na	na

UNDERSTANDING FORMALDEHYDE FORMATION AND DESTRUCTION PATHWAYS

Formaldehyde is the predominant intermediate in the combustion of natural gas and the highest concentration HAP in engine exhaust. Therefore, it is helpful to understand its formation and destruction pathways in order to better understanding the parameters which influence formaldehyde emissions from engines.

The oxidation or decomposition of methane to formaldehyde and other combustion products depends on temperature and the availability of oxidation radicals. Methane is one of the more difficult hydrocarbon compounds to decompose. The temperature at which it will react with oxygen is 1170 °F versus 860 °F for formaldehyde. Methyl radicals (CH_3) are formed via thermal decomposition of methane, hydrogen abstraction, or reactions with other radicals (OH, O, H, and HO_2). These methyl radicals react in one of three general paths, i.e., methyl radical oxidation, methyl radical/radical reaction, or methyl radical recombination. Each of these paths leads to the production of formaldehyde as shown below. (3)

Methyl Radical Oxidation

$CH_3 + O_2 = CH_3O + O$

$CH_3O + O_2 = CH_2O + HO_2$

$CH_3O + M^7 = CH_2O + H + M^7$

$CH_3 + H + CH_2O + H_2$

Methyl Radical/Radical Reactions

$CH_3 + O = CH_2O + H$

$CH_3 + OH = CH_2O + H_2$

Methyl Radical Recombination

$CH_3 + CH_3 = C_2H_6 \rightarrow C_2H_5 + H \rightarrow CH_2O$[8]

Methyl radicals oxidize to form methoxy radicals (CH_3O) under lean fuel conditions. The methoxy radicals further decay to form formaldehyde (CH_2O). The methyl radicals (CH_3) also react with O and OH radicals to form formaldehyde directly. The methyl radical-radical reactions are fast relative to the oxidation reaction and may tend to dominate when residence times are relatively short. In fuel rich mixtures, the methyl radicals can recombine to form higher order hydrocarbons, particularly ethyl radicals (C_2H_5) or ethane (C_2H_6) which

[7] M represents all collision partners, mostly methane (CH_4), active in thermal decomposition.

[8] Ethyl radicals break down or react with O or OH via several pathways to form formaldehyde.

breaks down further to form ethyl radicals. The ethyl radicals then either break down or react with O or OH to form formaldehyde via several possible pathways. (3)

Formaldehyde Dissociation

Formaldehyde reacts primarily with OH, H, and O radicals to produce formyl radicals. Formaldehyde may also dissociate in high temperatures by colliding with methane and other species (M) to form formyl, CO and H. These reactions are shown below:

$$CH_2O + OH = HCO + H_2O$$
$$CH_2O + H = HCO + H_2$$
$$CH_2O + O = HCO + OH$$

$$CH_2O + M = HCO + H + M$$
$$CH_2O + M = CO + H_2 + M$$

The reactions between formaldehyde and radical species are dominant in most cases. Based on this information, GRI has theorized that the air to fuel (A/F) ratio and mixing characteristics may be more important than temperature in the engine combustion chamber.

Studies on methanol-fueled automobile engines show the following trends on formaldehyde formation. It is reasonable to expect that similar trends may be observed for natural gas fired engines:

- Formaldehyde emissions increase as the A/F ratio is increased;
- Formaldehyde emissions decrease as the combustion/exhaust temperatures are increased; and
- Operating conditions that cause an increase in THC also result in higher formaldehyde emissions.(3)

ENGINE DESIGN AND POTENTIAL FORMADEHYDE EMISSIONS

The differences in formaldehyde emissions within engine families reflect the effect of differences in engine design, operating parameters, and maintenance history. The differences in formaldehyde emissions between engine families are discussed below. This information is based on GRI's latest report "Measurement of Air Toxic Emissions from Natural Gas-Fired Internal Combustion Engines," published in February 1996. The 16 engines tested included 13 unique models from the most common manufacturers i.e., Cooper Bessemer, Clark, Ingersoll Rand, and Waukesha. Engine models and test results were separated into five

categories based on design differences. As summarized in Table 2 above, these categories include the following:

- 2-stroke lean-burn,
- 2-stroke clean-burn (low NOx),
- 4-stroke lean-burn (direct injected and port injected or carbureted),
- 4-stroke rich-burn, and
- 4-stroke clean burn (low NOx).

2-Stroke Engines

2 stroke engines complete the power cycle in one revolution of the crankshaft. Fresh air sweeps the cylinder of exhaust gases during the cycle and 2-stroke engines operate with an overall A/F ratio that is greater than stoichiometric, i.e., fuel lean conditions. Thus, 2-stroke engines are classified as having lean-burn combustion. Newer models are designed to utilize turbochargers and high-energy ignition systems to achieve stable combustion at even higher A/F ratios. The higher A/F ratio lowers combustion temperatures and, thereby, reduces NOx formation. Due to the reduced NOx levels, these models are commonly called "clean-burn" engines. (3)

2-Stroke Lean-Burn Engines

A lean burn engine operates with an A/F ratio that is greater than stoichiometric and cannot be adjusted to operate with an exhaust O_2 concentration of less than 1 percent. A/F mass ratios range from 20:1 to 60:1 with exhaust temperatures ranging from 550 to 850 ° F.

The higher air content increases the heat capacity of the mixture in the engine cylinder which lowers combustion temperatures and results in more THC emissions. Formaldehyde emissions are also higher because there is less formaldehyde dissociation taking place at lower temperatures.

Two stroke lean burn engines are direct-injected, i.e., fuel is injected directly into the cylinder. As a result there is non-uniform mixing of air and fuel prior to combustion, and there is more apt to be concentration and thermal gradients in the combustion chamber. This is unlike the 4-stroke engine design which may have carbureted (premixed) fuel delivery systems. Because of the potential non-uniform mixing of the air and fuel, 2-stroke engines tend to have higher THC and formaldehyde levels than 4-stroke carbureted engines.(3)

2-Stroke Clean-Burn Engines

Engines that are designed to reduce NOx through combustion modifications are called "clean burn." Clean burn engines use turbochargers to force more air into the cylinder. The increased A/F ratio reduces bulk gas and

combustion temperatures, resulting in less NOx formation. However, the reduced temperatures also increase THC, CO, and formaldehyde emissions. By operating under very lean conditions, combustion temperatures are reduced and flame quenching is increased resulting in a larger amount of partially oxidized fuel (including formaldehyde) leaving the cylinder. (3)

4-Stroke Engines

A 4-stroke engine completes the power cycle in two full revolutions of the crankshaft. The three basic configurations i.e.,: 4-stroke lean-burn, 4-stroke rich-burn and 4-stroke clean-burn are described below.

4-Stroke Lean-Burn

Four-stroke lean-burn engines are available in two basic designs: direct injected and premixed (carbureted or port injected). The *direct injected* 4-stroke lean burn engines have larger temperature and concentration gradients between the combustion zone and the remainder of the cylinder. The combustion zone is fuel rich and essentially "hotter". This is similar to conditions in a rich burn engine. The *pre-mixed* engine types combust a homogeneous air/fuel mixture, which leads to a cooler combustion zone. As discussed earlier, formaldehyde emissions increase as bulk cylinder temperatures decrease. Therefore, the formaldehyde emissions for the premixed lean burn engine are significantly higher than for direct injected engines as shown in Table 5.

Formaldehyde emissions from 4-stroke lean-burn engines are expected to be lower than from 2-stroke lean-burn engines. This is due to better mixing, and reduced temperature and fuel gradients in the cylinder. Also, the residence time of combustion products is longer in a 4-cycle engine. (3)

4-stroke lean-burn engines have higher formaldehyde emissions than 4-stroke rich-burn engines as the increased A/F ratio in the lean-burn design reduces combustion temperatures. (3)

4-Stroke Rich burn

Among the five engine classes, the lowest formaldehyde emissions were measured for the 4-stroke rich-burn engines. This is the result of the high combustion and exhaust temperatures associated with the lower A/F ratio. Rich burn engines operate with an A/F ratio that is near stoichiometric, or fuel-rich, and have an exhaust O_2 concentration ranging from nearly zero to five percent. A/F ratios typically range from 16:1 to 20:1. Because of the low O_2 levels, combustion temperatures, are higher than for lean burn engines. At the higher temperatures associated with fuel rich combustion, formaldehyde dissociation

reactions are more likely to occur. Also, there is less likely to be unoxidized or partially oxidized fuel in poorly mixed zones. (3)

4-Stroke Clean Burn

Newer 4-stroke engines are often designed with very high A/F ratios to minimize NOx formation, similar to 2-stroke engine designs. Four-stroke clean-burn engines can be classified as "injected" or "premixed". The injected design may have higher fuel concentration gradients, leading to nonuniform temperature in the combustion chamber. The cool areas in the combustion chamber can increase formaldehyde emissions due to less formaldehyde dissociation.

Four-stroke carbureted engines premix the air and fuel prior to charging the combustion chamber. Therefore the temperature is more uniform. Compared to uncontrolled 4-stroke engines, the premixed clean-burn design exhibits lower combustion and exhaust temperatures due to higher A/F ratio. Therefore, formaldehyde emission levels may tend to be higher than for comparable uncontrolled engines.(3)

Precombustion chambers (PCCs) used in many clean-burn engine designs to reduce NOx emissions, provide a fuel-rich mixture for ignition, raise temperature, and thus might be expected to reduce formaldehyde emissions. This was not found to occur, however, as improved mixing and high A/F ratios appear to be more important for impacting formaldehyde emissions.(3)

Table 5

ENGINE DESIGN CATEGORIES

	HCHO Emissions g/hp-hr
4-STROKE CLEAN-BURN (LOW-NOx)	**0.23**
2-STROKE LEAN BURN	**0.18**
2-STROKE CLEAN-BURN (LOW NOx)	**0.16**
4-STROKE LEAN-BURN	
PREMIXED	**0.14**
DIRECT INJECTED	**0.04**
4-STROKE RICH-BURN	**0.10**

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OTHER FACTORS INFLUENCING EMISSIONS OF FORMALDEHYDE FROM GAS ENGINES

Using GRI's FTIR test data, other engine operating parameters were evaluated to determine their impact on formaldehyde emissions. The factors considered included add-on controls, torque, speed, cylinder temperature, A/F ratio, cylinder bore and stroke, and ignition timing. It was not possible to vary certain parameters such as speed and A/F ratio over a wide enough range to distinguish emissions changes associated with their impact from normal engine variability. Of the operating factors studied, torque had the strongest influence on formaldehyde emissions.(3)

Effect of Exhaust Emission Controls

The impact of emission controls such as clean-burn design were discussed above. Limited data collected on catalytic converters suggests that formaldehyde emissions may be reduced with certain oxidation catalysts. Data was not available for selective catalytic reduction (SCR) systems as ammonia levels interfered with FTIR measurements. The non-selective catalytic reduction catalyst (NSCR) showed reduced formaldehyde levels although formaldehyde was already low to begin with as the NSCR are designed for operation at very low O_2 levels.(3)

Effect of Torque

Formaldehyde emissions increase as engine torque decreases. This is due to lower cylinder gas temperature which reduces oxidation of hydrocarbons like formaldehyde.

If a "full-load" emission factor were chosen to calculate mass emission rates for permitting purposes, it would underestimate emission rates at off-load conditions and potentially create a compliance issue if the unit operated at off-load conditions.

Effect of A/F ratio

Exhaust O_2 levels may be used as a surrogate measure of the actual A/F ratio in the combustion cylinder. As expected, formaldehyde emissions increase with increasing exhaust O_2. Higher A/F ratios increase the heat capacity of the combustion mixture in the cylinder and lead to reduced bulk gas temperatures. As the temperature decreases formaldehyde destruction is decreased. Also at very high A/F ratios, flame quenching may occur, resulting in significant quantities of partially oxidized fuel (frequently formaldehyde) being emitted from the engine. (3)

Effect of Maintenance

Engines in service within gas plants e.g., prime movers, were found to have higher emissions of formaldehyde than comparable engines used in storage reservoirs or pipeline service. This may be attributed to poorer maintenance schemes for these in-plant engines. Many gas plants don't perform maintenance on the prime mover engines until it is absolutely necessary, whereas pipeline engines appear to receive more attention. Therefore, "maintenance pays" not only in terms of savings incurred from lower fuel use, but also in terms of lower formaldehyde emissions. (7)

CONCLUSIONS

In conclusion, formaldehyde emissions from natural gas-fired IC engines should be quantified for regulatory compliance purposes. Emission factors which best represent the specific engines being evaluated should be used whenever possible. Factors which are believed to influence actual emissions include engine design, emission controls, operating parameters and maintenance history.

GRI-sponsored research has provided much information over the last 2 years. Additional information is still needed, however, particularly for engine models that show the highest emission rates and for which there is little information (i.e., 2-stroke clean burn; 4-stroke lean burn , and 4-stroke clean-burn designs). In addition, strategies to reduce emissions through process/combustion modifications and add-on controls should be evaluated.

REFERENCES

1. Environmental Protection Agency (EPA), "Compilation of Air Pollutant Emissions Factors," AP-42, Fifth Edition, January 1995.

2. *Clean Air Permits, Manager's Guide to the 1990 Clean Air Act,* Washington, D.C: Thiompson Publishing Group, 1995.

3. Shareef, Ferry, Gundappa, Leatherwood, Ogle, and Campbell, "Measurement of Air Toxic Emissions from Natural Gas-Fired Internal Combustion Engines at Natural Gas Transmission and Storage Facilities," Volume I Topical Report prepared for Gas Research Institute, GRI-96/0009.1, Radian Corporation, February 1996.

4. Shareef, Ogle, LaCosse, "Fourier Transform Infrared (FTIR) Method Validation at a Natural Gas-Fired Internal Combustion Engine," Topical Report prepared for Gas Research Institute, GRI-95/0271, Radian Corporation, December 1995.

5. Patrick, David, R., *Toxic Air Pollution Handbook,* New York: Van Nostrand Reinhold, 1994.

6. New Mexico Environmental Department Air Pollution Control Bureau, Memo: Guidance for Establishing Monitoring required under 40 CFR70 for Title V Permits - "Formaldehyde Monitoring for Engines" November 13, 1995.

7. Telephone Communications between James M. Evans, Project Manager, Gas Research Institute (GRI), Chicago, Illinois, and Daphne V. Economou, Liaise Environmental, Inc., July 1996.

8. Telephone Communications between Kathy R. Ferry, Radian Corporation, Austin. Texas, and Daphne V. Economou, Liaise Environmental, Inc., September 13, 1996

9. EPA Air Emissions Species Manual, Volume I, Second Edition, EPA-450/2-90-001a, January 1990.

10. Telephone Communications between James M. McCarthy, Project Manager, Gas Research Institute (GRI), Chicago, Illinois, and Daphne V. Economou, Liaise Environmental, Inc., August 27, 1996, and September 12, 1996.

Development of Regenerative Catalytic Process for Purification of Sulfur Containing VOC Flows

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ABSTRACT

Vent gases from storage and handling of petroleum products often contain both various organic compounds and compounds of sulfur, such as hydrogen sulfide, mercaptans, etc., which create odor problems. This paper deals with a method for treatment of such emissions using catalytic oxidation in a reverse-flow reactor that combines catalytic oxidation reaction with regenerative heat recovery. Research results are reported that were used for design and operation of a catalytic oxidation system installed at an asphalt production facility and loaded with an alumina supported copper-chromium catalyst. The system can be also used for the treatment of tail gases generated by Claus units.

Oxidation of H_2S and other sulfur-containing compounds causes the catalyst poisoning. The deactivation was found to proceed relatively slowly, but after three months of operation the catalyst had lost over 90 % of its activity. This can be partially compensated by the ability of the reverse-flow reactor to increase operating temperature along with the catalyst deactivation. This unique feature of the reactor is illustrated by numerical simulation.

Naturally, this compensation effect has its limitations, thus the need for the catalyst regeneration was recognized. The procedure for *in situ* thermal regeneration of the catalyst was developed, and the results of regeneration tests are reported. It was important to determine an optimum temperature of regeneration to do it quickly and without catalyst sintering at elevated temperatures.

Another aspect of the problem involves emission of sulfur oxides produced by oxidation reactions. The upper catalyst operating temperature limit was established to minimize SO_3 formation. Emitted sulfur oxides are absorbed by caustic solution in a downstream froth scrubber.

INTRODUCTION

Large streams of gases containing sulfur compounds, often mixed with volatile organic compounds (VOC), are released at numerous plants in various industries, such as pulp and paper, wastewater biotreatment, natural gas and petroleum processing, synthetic fibers and pharmaceuticals. For instance, H_2S is released after Claus process units that recover sulfur found in crude oil and natural gas. Various methods have been developed to remove sulfur from waste gases: thermal and catalytic oxidation, biofiltration, adsorption and absorption methods.

In most cases these waste gases have low temperature and need to be preheated for thermal or catalytic incineration. While the heat of reaction is usually recuperated, auxiliary fuel is used to preheat gases, such ash tail gases of Claus process units, before contacting with catalyst bed [1]. This makes regenerative catalytic oxidizers (RCOs) a natural choice for purifying those gases.

Sulfur is known to poison most VOC oxidation catalysts. This makes it crucial to choose an appropriate catalyst, especially in applications where both VOC abatement and sulfur compounds removal must be realized.

An air pollution control system was designed and built by Monsanto Enviro-Chem at Emulsicoat asphalt production facility in Urbana, IL, to treat vent gases containing VOCs and H_2S. The system includes an RCO loaded with copper-chromium catalyst to convert combustible compounds into CO_2, H_2O and SO_2, and a scrubber to capture sulfur oxides. This paper describes the RCO design and performance and discusses various aspects of the catalyst operation.

UNIT DESIGN AND OPERATION RESULTS

The customer requested replacement of an existing activated carbon adsorption unit because of large carbon replacement costs. The new system was to treat vent gases with variable flow rate and VOC concentrations (Table 1).

Table 1.
Conditions of plant operation

Flow conditions	Flow rate, m^3/h	Concentration of hydrocarbons (C_4-C_9), g/m^3	Adiabatic temperature rise, °C
Maximum	1700	4.7	167
Normal # 1	2500	1.97	70
Normal # 2	1700	1.44	51
Minimum	1700	0.14	5

The vent gas temperature varied from 25 to 45°C. At maximum and normal flow conditions the exhaust gas may contain up to 1,000 of H_2S, as well as sulfur organics. Hydrocarbons are present in the following proportions:

Linear C_3/C_4	55 %
Linear $C_7/C_8/C_9$	25 %
Aromatic $C_7/C_8/C_9$	20 %

The customer requirements included:

- > 95 % destruction at low concentrations and > 98 % destruction at higher concentrations;
- Start up every morning following a 7 - 10 hour production shutdown with minimal operator involvement;
- Start up with minimum energy consumption after 1 - 2 days (weekend) production shutdown.

DynaCycle® RCO technology was proposed by Enviro-Chem to meet these requirements. RCO advantages, fundamental principles and examples of commercial applications are discussed in [2-4,9]. A flow diagram of the system is given in Fig. 1. The vent gas passes through Brinks® filters 1, then is directed by valve 2 into the upper or lower bed of preheated ceramic material which serves to heat up the incoming gas to the preset temperature. Then the gas enters the fixed bed of catalyst where VOCs are oxidized and heat is released. The purified air stream exits the catalyst bed through another bed of ceramic packing, giving up its thermal energy to the solid material. Then this energy is reused to preheat the gas in the next phase of the cycle, when the gas flow through the beds is reversed. Through outlet valve 4 the gas flow passes to the DynaWave® froth scrubber 5 where sulfur oxides and sulfuric acid mist are removed by diluted caustic solution.

The process control includes a simple system for choosing an appropriate time for flow reversal in response to the minimal temperature in the catalyst bed. Also controlled is the supply of natural gas to maintain the catalyst temperature at low VOC concentrations. To prevent catalyst overheating and minimize SO_3 formation, ambient air supply before the catalyst is provided for.

The oxidizer was designed on the basis of computer simulation using one-dimensional mathematical model discussed in [2-4]. This model accounts for chemical reaction, heat transfer between surface of solid particles and the bulk of the gas phase, heat capacity of the solid phase, and mass and heat transfer by convection. Reaction kinetics parameters obtained from experiments were directly used for reactor simulation.

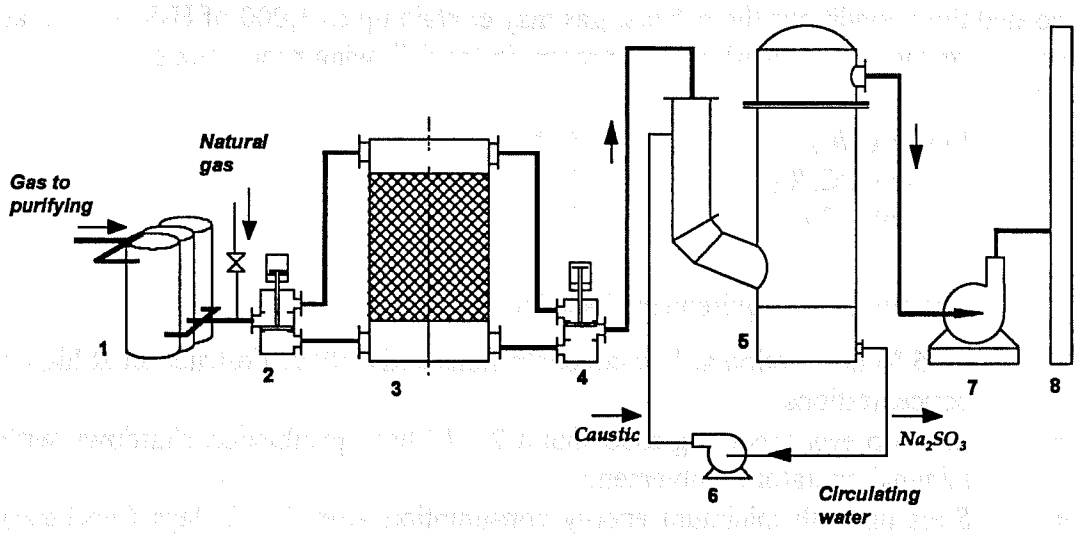

Figure 1. Asphalt fume treatment system. 1: Brinks filters, 2: inlet valve, 3: DynaCycle reactor, 4: outlet valve, 5: DynaWave scrubber, 6: water circulation pump, 7: fan, 8: stack.

The commercial catalyst, ICT-12-8, contains primarily copper chromite on γ-alumina. It has well developed internal porous structure and large internal surface area, > 100 m^2/g. As an example of the catalyst activity in VOC destruction, Matros et. al. reported that the rate of oxidation of 0.2 % of butane in air on ICT-12-8 is equal to 0.11 $cm^3/(g \cdot s)$ at 300°C, and 0.48 $cm^3/(g \cdot s)$ at 400°C [4]. The catalyst has demonstrated good activity and lifetime in a large number of reverse-flow VOC oxidation units [3,4].

The system has been in operation since 1993. It attains removal efficiency of 99 %. Pressure drop at normal flow rate is approximately 200 mm W.C. The average cycle duration is 25 to 30 min. The catalyst temperature is typically ranging from 450 to 550°C.

The catalyst oxidized H_2S and other sulfur-bearing compounds vaporized from asphalt tanks into CO_2, H_2O and sulfur oxides, both SO_2 and SO_3. The latter combines with water vapor to form sulfuric acid at the unit outlet. Sulfur trioxide is highly corrosive and is considered to be a much more dangerous catalyst poison than other sulfur compounds that can destroy both active component and alumina support [5]. Authors of [8] reported that up to 3 % of H_2S is converted to SO_3 at 300-400°C at stoichiometric conditions, and can be higher at oxygen excess. Heisel et. al. [1] also noted that oxygen control is important in Claus tail gas incineration units to prevent SO_3 production.

Since oxygen content could not be controlled in the vent gas treatment application , the only way to reduce SO_3 content is to maintain lower temperatures in the catalyst bed, where SO_3 formation is less likely. A maximum temperature limit of 590°C was set where no visible acid mist was usually observed.

CATALYST DEACTIVATION AND REGENERATION

To ensure long-term unit operation it was necessary to develop a procedure for its regeneration *in situ*, without having to shutdown the unit. Generally, a catalyst regeneration, if at all possible, is performed using thermal treatment or washing with water or some sort of regenerative solution [5].

There is a substantial body of literature dealing with the interaction of copper-chromite VOC oxidation catalysts with sulfur. One can see from the review by Spivey and Butt [2] that both the rate of deactivation and regeneration possibilities strongly depend on the catalyst composition. More pertinent details could be found in papers by Russian authors discussing catalysts similar to that used in Emulsicoat unit.

Mulina et. al. [7] studied effect of 0.1 % of SO_2 on the performance of eight catalyst samples in CO oxidation. The authors observed poisoning, suggested its mechanism that includes two routes, one reversible and another irreversible, and determined kinetic parameters of deactivation. They also observed partial restoration of the catalyst activity at 600°C. Oxidation of H_2S in a stoichiometric mixture with oxygen at 300°C was investigated by Khanmamedov et. al. [8]. Sulfur compounds were found to cause reversible destruction of copper chromite accompanied with activity decrease. Sulfur was found on the surface in the form of copper sulfate (surface sulfation was also found in [7] and [10]). The authors suggested the reaction mechanism which implied includes no irreversible poisoning of the catalyst. Matros et. al. [4] reported a model of reversible deactivation of copper-chromite catalyst by SO_2 during CO oxidation, and used this model for simulation of reverse-flow reactor operation. Possibility of thermal regeneration of the catalyst at or over 700°C was suggested. In another study, Kovalenko et. al. [10] presented experimental results of ICT-12-8 operation in oxidation of methane in air mixed with 0.05 % of SO_2. Deactivation was found to be retarded with the temperature increase from 500 to 700°C.

In our studies we used samples of poisoned catalyst taken from the center of the catalyst bed of the commercial unit. After about two months of operation, the catalyst contained 3 to 5 % sulfur as sulfate ions and retained only from 7 to 10 % of its initial activity (which nevertheless allowed the oxidizer to perform satisfactorily).

Catalyst activity was determined using a catalyst tester from CATACON Co. (Novosibirsk, Russia). The unit includes a system for preparing a mixture of 1 % propane in air and isothermal gradientless reactor with external recycle which accommodated commercial-size rings. A GC was used for gas analysis at the reactor inlet and outlet. Activity of the catalyst was expressed as a first-order reaction rate constant. More details on experimental procedure were given in [9].

The catalyst was regenerated in air at temperatures from 600 to 800°C. Results of regeneration tests are presented in Figs. 2 and 3. In these figures, the rate constant at 300°C is used as a measure of the catalyst activity. At 700°C, the catalyst slowly recovered its activity up to 80 % of the activity of fresh sample (Fig. 2). Activity of a fresh sample decreased slightly in the first 20 hours, then stabilized. A calcination temperature increase to 800°C made regeneration faster, but then the activity declined, possibly because of sintering of alumina support (Fig. 4). Fresh catalyst activity also declined, and eventually converged with the activity of regenerated samples. These data agree with the results obtained in [10] where activity of ICT-12-8 decrease by 25 % after 10 hours treatment at 750°C. Almost complete regeneration at 700°C was achieved also with the catalyst sample that was in service for 2.5 years and underwent multiple regeneration sessions.

As a result, the procedure for in situ regeneration of catalyst was developed. It involves relatively long (8 hr. or longer) exposure to a temperature of around 700°C, preferably in a sulfur free atmosphere.

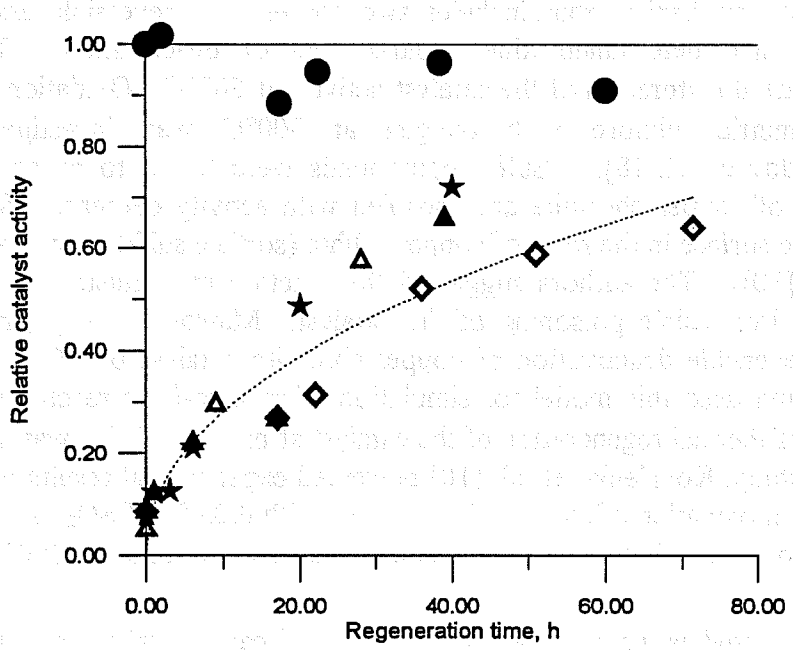

Figure 2. Regeneration of poisoned catalyst at 700°C. ● - sample of fresh catalyst; other symbols - different samples of poisoned catalyst.

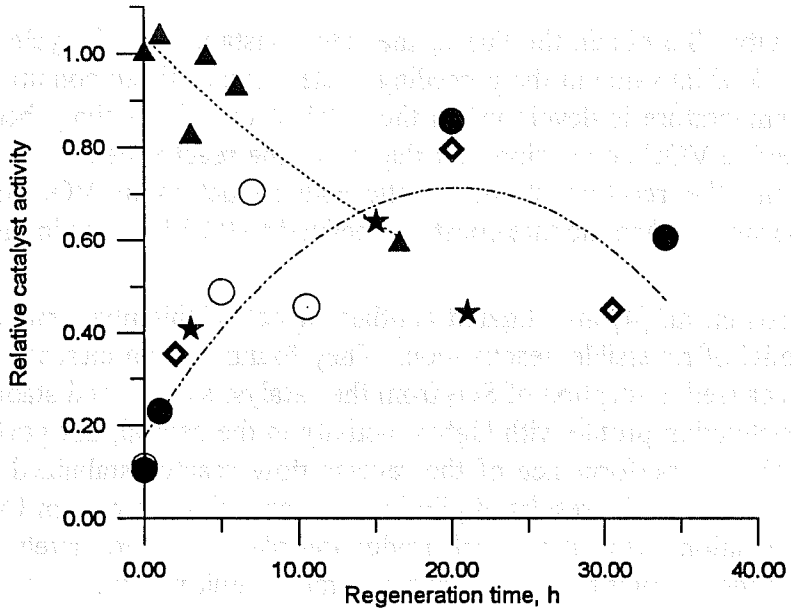

Figure 3. Regeneration of poisoned catalyst at 800°C. ▲ - sample of fresh catalyst; other symbols - different samples of poisoned catalyst.

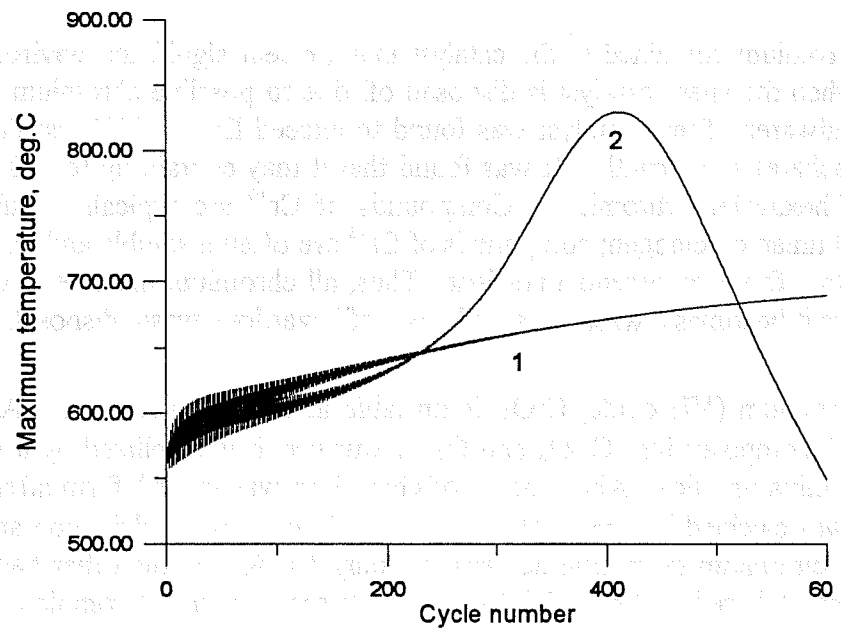

Figure 4. Simulation of development of maximum temperature in a reverse-flow reactor with stable (1) and deactivating (2) catalyst.

The RCO has a unique ability of keeping high VOC destruction efficiency when the catalyst activity declines. Generally, lower catalyst activity causes higher maximum temperature in the catalyst bed, up to a certain limit [3,4]. Fig. 4 shows a simulation example that shows the maximum temperature changes during the convergence of periodic regime. Line 1 in Fig. 4 was calculated with constant

catalyst activity. To obtain the line 2, the rate constant in each cycle was made equal to 98 % of its value in the preceding cycle. Under these conditions, higher maximum temperature is developed in the catalyst until its activity becomes too low for effective VOC conversion. At that point the reactor begins to cool down and eventually the reaction stops. Noticeable reduction in VOC destruction efficiency occurred when the rate constant declined to 0.25 % of its initial value.

Matros et. al. [4] investigated another aspect of this phenomenon using a dynamic model of reversible deactivation. They found that an increase in catalyst temperature caused desorption of SO_2 from the catalyst surface and stabilization of the axial deactivation profile with highest activity in the central, hot portion of the bed. Accordingly, performance of the reverse-flow reactor stabilized too. The monograph [4] quotes the results of piloting a reverse-flow reactor in CO removal from agglomeration gases at a steel production plant. Unfortunately, we could not test this concept since the maximum temperature limit was imposed.

CATALYST DISPOSAL

Chromium contained in the catalyst may present significant environmental concern when the spent catalyst is disposed of, due to possible chromium transfer into groundwater. Fresh catalyst was found to exceed EPA TCLP test limit (5.0 mg/l in leachate) significantly. It was found that it may contain up to ~ 0.9 % by weight of hexavalent chromium. Compounds of Cr^{+6} are typically soluble and known as human carcinogen; compounds of Cr^{+3} are often insoluble and non-toxic, and in certain forms an essential nutrient. Thus, all chromium must be in trivalent form before it becomes a waste to avoid costs of hazardous waste disposal.

Chromium (VI) oxide, CrO_3, is unstable at high temperatures. At about 250°C, it decomposes into Cr_2O_3 and O_2. However, it is stabilized by a support such as alumina or silica. About 55 % of chromium was in Cr^{+6} form after Cr_2O_3 on Al_2O_3 was calcined in oxygen at 550°C [12]. In our tests, calcination at 750°C resulted in chromium extraction decrease by only 10 %. On the other hand, Cr^{+6} can be completely reduced by CO [12]. Our tests showed almost complete

Table 2.

Chromium (VI) content and results of TCLP testing of ICT-12-8 catalyst.

Catalyst sample	Cr^{+6}. μg/g	TCLP test data, mg/l
Fresh	8,000 - 13,000	360
1,000 hr. in α-pinene oxidation unit	4,000 - 4,800	145 - 160
3 months in asphalt fume treatment unit	155	10 - 15 (estimate)
6 months in asphalt fume treatment unit		15.0
12 months in asphalt fume treatment unit		5.0

reduction of Cr^{+6} by hydrogen in an oxygen-free atmosphere.

In actual process conditions, there are both oxidizing (oxygen) and reducing agents (organic compounds and H_2S). It turns out that both the Cr^{+6} content and level of leachable chromium decrease in time. Data in Table 2 imply that the spent catalyst after a year or more would be qualified as a non-hazardous waste. Since the catalyst is still in the unit, the final check is yet to be done.

CONCLUSIONS

The air pollution control system composed of a regenerative oxidizer and froth scrubber successfully removes both VOCs and sulfur-bearing compounds from an asphalt making facility vent gases since 1993. It replaced an activated carbon adsorption system to bring greatly reduced operating cost, low energy consumption, easy handling of variable flow rates and concentrations of pollutants, and easy start up after overnight or weekend shutdowns within minutes.

Copper-chromium catalyst loaded into the oxidizer has demonstrated its ability to treat sulfur-containing gases. Though sulfur poisons the catalyst, this poisoning can be reversed by thermal treatment of the catalyst at over 700°C. High thermal efficiency of the RCO allows *in situ* regeneration to proceed with minimum energy cost. With such periodic regeneration, the catalyst is expected to work three to five years before it must be replaced.

While fresh catalyst contains high amounts of hexavalent chromium, its operation in a VOC control unit causes gradual reduction of C^{+6} into Cr^{+3}. It is expected that after about one year of operation the spent catalyst can be qualified as a non-hazardous waste.

There are still certain aspects of this technology that need to be further investigated to improve the understanding of processes occurring in the reactor: actual rates of oxidation of H_2S, COS, CS_2 and other compounds that can be encountered in similar applications, actual rates of deactivation by different sulfur compounds, and maximum number of deactivation/regeneration cycles that the catalyst can endure. It is important to better define the maximum and minimum temperature limits for successful long-term operation with minimum SO_3 release.

Nevertheless, the knowledge accumulated to date and the commercial experience make it possible to suggest application of copper-chromium catalyst for removal of odorous sulfur compounds in different industries, either in RCO or in traditional, steady-state catalytic incinerators.

REFERENCES

1. Heisel, M., Linde, G., Marold, F. "Sulphur Removal and Recovery from Gases," *Linde Reports on Science and Technology*, no. 35 (1985).

2. Matros, Yu. Sh., Bunimovich, G. A., Patterson, S. E., and Meyer, S. F. "Is it Economically Feasible to Use Heterogeneous Catalysts for VOC Control in Regenerative Oxidizers?" *Catalysis Today*, **27**, 303-313 (1996).

3. Matros, Yu. Sh., Noskov, A. S., and Chumachenko, V. A. "Progress in Reverse-Process Application to Catalytic Incineration Problems," *Chem. Eng. Proc.*, **32**, 89-98 (1993).

4. Matros, Yu. Sh., Noskov, A. S., and Chumachenko, V. A. *Kataliticheskoe Obezvrezhivane Otkhodyashchikh Gasov Promyshlennykh Proizvodstv* (Catalytic Purification of Industrial Off-Gases). Novosibirsk, Nauka, Sibirskoe Otdeleniye, 1991. *(in Russian)*

5. Chen, J., Heck, R. M., and Farrauto, R. J. "Deactivation, Regeneration and Poison-Resistant Catalysts: Commercial Experience in Stationary Pollution Abatement," *Catalysis Today*, **11**, no. 4, 517-546 (1992).

6. Spivey, J. J. and Butt, J. B. "Literature Review: Deactivation of Catalysts in the Oxidation of Volatile Organic Compounds," *Catalysis Today*, **11**, no. 4, 465-500 (1992).

7. Mulina, T. V., Filipov, A. V., and Chumachenko, V. A. "CO Oxidation over $CuCr/Al_2O_3$ Catalysts in Presence of SO_2," *React. Kinet. Catal. Lett.*, **37**, no. 1, 95-100 (1988).

8. Khanmamedov, T. K., Kalinkin, A. V., Kundo, N. N., and Novopashina, V. M. "XPS Studies of Active Surface of Al-Cu-Cr Catalyst for Oxidation of Tail Gases from Sulphur Production," *React. Kinet. Catal. Lett.*, **37**, no. 1, 83-88 (1998).

9. Matros, Yu. Sh., McCombs, D. E., Strots, V. O., Bunimovich, G. A., Roach, C. R. "Catalytic Reverse-Process for VOC Control: Experimental Data and Reactor Simulation," in: *Environmental Issues and Solutions in Petroleum Exploration, Production and Refining.* PennWell Books, 1994, 44-53.

10. Kovalenko, O. N., Tsyrul'nikov, P. G., Ivanov, D. P., Starostina, T. G., Gogin, L. L. Gul'kova, L. G., and Kudrya, E. N. "Dynamics of the Activity of Deep Oxidation Catalysts Under the Extreme Conditions," *Abstracts of 2nd Int. Conf. on Unsteady-State Processes in Catalysis.* St. Louis, USA, 1995.

11. James, B. R. "The Challenge of Remediating Chromium-Contaminated Soil", *Environ. Sci. Technol.*, **30**, no. 6, 248A - 251A (1996).

12. Weckhuysen, B. M., De Ridder, L. M., Schoonheydt, R. A. "A Quantitative Diffuse Reflectance Spectroscopy Study of Supported Chromium Catalyst," *J. Phys. Chem.*, **97**, 4576-4763 (1993).

Emissions and Ambient Impacts from Insignificant Activities

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The Title V operating permit program provides for some types of sources to be identified as insignificant activities. Little or no quantification of emissions and no assessment of ambient impacts is required of these sources for a Title V permit.

There are two principal classes of insignificant activities: activities which meet specific emission limits, and activities which satisfy emission-related criteria such as heat input, size, or vapor pressure. The federal operating permit program, 40 CFR 71, specifies that sources meeting specific emission limits are insignificant, while many state programs specify both specific emission limits and and emission-related criteria as insignificant. Emissions and impacts from both classes of insignificant activities are assumed to be negligible. However, based on our observations, this assumption for the most part has not been rigorously tested.

The authors have performed detailed emissions calculations for common oil and gas related insignificant activities of both classes based on the 40 CFR 71 criteria and the New Mexico insignificant activities list. In order to quantify emissions from these activities, their ambient impacts were modeled. Modeled impacts were compared to appropriate air quality standards and threshold limit values (TLVs) in order to assess the health threat of these activities.

Based on this limited study it appears that many of the commonly identified insignificant activities meeting emission-related criteria also meet the emission limits of the federal operating permit program and that sources meeting either of these criteria are unlikely to affect health or the environment.

DATA SOURCES

In general, there are two classes of insignificant activities —

- Activities which satisfy specific emission limits, and
- Activities which satisfy an emission-related criteria such as size, heat input,vapor pressure, or horsepower.

Emissions from a total of six common oil and gas related insignificant activities of both classes are evaluated in this study. Source types 1 and 2 are sources of the first class, having emission rates defined in 40 CFR 71 [1]. Source types 3 through 6 are of the second class, meeting specified emission related criteria such as heat input, size, vapor pressure and horsepower as established in the New Mexico Environment Department (NMED) Air Quality Bureau (AQB) list of insignificant activities [2] [8].

Table 1

Types of Insignificant Activities Examined in this Study

Activity Type	Description
1	Sources emitting 1 ton/yr of non-HAP regulated pollutants
2	Sources emitting 1000 lbs/yr of common HAPs
3	Natural gas fueled heaters of 5 MMBtu/hr heat rate
4	Distillate fueled heaters of 1 MMBtu/hr heat rate
5	1000 barrel tank containing a liquid with a vapor pressure < 10 mm Hg
6	500 gallon tank containing a liquid with a high vapor pressure

TYPES 1 AND 2

Source types 1 and 2 are established in accordance with the Federal Operating Permits Program Rule, 40 CFR 71 [1]. Part 71 specifies as insignificant any sources with a maximum emission rate of 1 ton/yr for regulated air pollutants other than Hazardous Air Pollutants (HAPs), or a maximum emission rate of 1000 lbs/yr, or the section 112(g) de minimis level of any HAP (40 CFR 71.5 (g)(2)) [1]. Type 1 is a source which emits 1 ton/yr of a regulated air pollutants other than HAPs which include nitrogen oxides (NOx), carbon monoxide (CO), volatile organic compounds (VOCs), sulfur dioxides (SO_2), total suspended particulates (TSP), and particulate matter less than 10 micrometers in diameter (PM-10). Type 2 is a source which emits 1000 lbs/yr of common substances in the oil and gas industry which are HAPs. The HAPs included in this study are benzene, hexane, ethylene glycol, toluene, ethyl benzene, xylenes, methanol, trichloroethlene, and formaldehyde, all of which can be emitted from industrial and oil and gas related sources.

TYPES 3 AND 4

Essentially all industrial facilities, including oil and gas production and transportation facilities, have numerous small heating units. The New Mexico insignificant activities list identifies

as insignificant gas-fueled combustion units of less than or equal to 5 million British thermal units per hour (MMBtu/hr) design heat rate (type 3) and distillate-fueled combustion units of less than or equal to 1 MMBtu/hr design heat rate (type 4). To be insignificant in New Mexico, these types of combustion units must be used for heating for personal comfort or generating domestic hot water. However, the use of the units does not affect their potential emissions or ambient impacts.

TYPES 5 AND 6

Applications for operating permits for 36 natural gas facilities owned by six operators and located in the Permian and San Juan Basins of New Mexico were reviewed to identify common sources meeting one or more of New Mexico's criteria for insignificance. The two most common such sources were also included in this study as source types 5 and 6.

Table 2 below summarizes the top five common insignificant sources at those facilities and the number of occurrences of each.

Table 2
Occurrences of Insignificant Sources

Activity	Occurrences
Lube and waste oil tanks	120
Glycol tanks	69
Corrosion inhibitor tanks	40
Diesel fuel tanks	20
Solvent tanks	19

These most common sources were all considered insignificant either because they involve liquids with a vapor pressure less than 10 mm Hg (0.20 psi), or tank volumes less than 500 gallons as specified in the New Mexico insignificant activities list [2]. The basis for the vapor pressure specification is that 40 CFR 68 (promulgated pursuant to §112(r) of the Clean Air Act) which presumes that substances with a vapor pressure less than 10 mm Hg are not volatile and thus do not present a hazard due to aerial releases [3] [7].

The basis for the tank volume specification is the assumption that small tanks are unlikely to have substantial emissions, regardless of their contents. Substances with very high vapor pressures are unlikely to be kept in vented, fixed-roof tanks because the losses would be substantial. Odorants, low-boiling gas fractions, and highly volatile solvents will be kept in sealed vessels to control losses and costs. This assumption is supported by our observations. The average vapor pressure we observed of substances stored in tanks of 500 gallons or less was 0.25 psia, and the maximum was 1.2 psia.

This study evaluates emissions from a very large tank of 42,000 gallons (1000 barrels) containing a liquid with a vapor pressure of 10 mm Hg (type 5). This study also considers emissions from a 500 gallon horizontal tank containing gasoline of Reid vapor pressure (RVP) 13, or 6.6955 psi @ 59 °F (type 6).

EMISSION CALCULATIONS AND PARAMETERS

Table 3 below summarizes the emission rates of regulated pollutants including common HAPs from each studied source type.

Table 3

Emissions Rates of Regulated Pollutants (in lbs/yr)

	Source Type					
Pollutant	1	2	3	4	5	6
NOx	2000		4555	1314		
CO	2000		964	333		
VOC	2000		237	26	558	377
SO2	2000		26	8.76		
TSP	2000		543	131		
PM-10	2000		543	131		
HAPs						
Benzene		1000	0.088		558	377
Hexane		1000			558	377
Ethylene Glycol		1000			558	377
Toluene		1000	0.27		558	377
Ethyl Benzene		1000			558	377
Xylenes		1000	0.39		558	377
Methanol		1000			558	377
Trichloroethlene		1000			558	377
Formaldehyde		see text	0.37	3.50		

Emissions from source types 1 and 2 are defined by regulation as 1 ton/yr non-HAP pollutant and 1000 lbs/yr HAPs, respectively. The first 8 HAPs listed here are common substances which are used, stored, or generated in the oil and gas industry. Formaldehyde is commonly generated by combustion sources, so ambient impacts were not evaluated here because the emission rate is typically 3 orders of magnitude less than the emission rate of NOx. For example, an engine large enough to emit 1000 lbs/yr formaldehyde would emit about 450 tons/yr of NOx. Such a source would not be considered insignificant. However, ambient impacts from formaldehyde emitted by combustion sources 3 and 4 were considered here.

Emissions from source types 3 and 4, small combustion sources, were calculated using EPA's Compilation of Air Pollution Emission Factors, AP-42 [4]. The gaseous fuel was assumed to

have a nominal heating value of 1000 Btu/cf, while the distillate fuel was assumed to have a heating value of 19,300 Btu/lb.

Many other common oil and gas-related sources meet the emission-related criteria of the New Mexico insignificant activities list. For example, small portable engines commonly used for power, lighting, pumping, etc. are considered insignificant if their horsepower is less than specific thresholds that depend on fuel type. Emission from these units would vary greatly, and are not considered here.

Sources 5 and 6 are tanks containing liquids of vapor pressure less than 10 mm Hg and tanks smaller than 500 gallons. Annual emissions from these sources were calculated using EPA's TANKS3 software with typical input values for the Permian Basin, assuming Midland-Odessa, TX meteorology. Short-term emission rates were not addressed.

The 1000 bbl tank was assumed to be a cone roof tank of approximately square dimensions, white roof and shell in good condition, with 18 turnovers per year and breather vents set at ± 0.03 psi. This hypothetical tank is larger and has more turnovers than the observed oil and glycol tanks considered in this study.

The 500 gallon tank was assumed to be a horizontal tank of approximately square dimensions, white roof and shell in good condition, with 26 turnovers per year and breather vents set at ± 0.03 psi. This hypothetical tank has more turnovers than typical observed small tanks, and would be considered a very busy tank for small-scale fueling operations.

As a very conservative assumption, the HAP emission rates of sources 2, 5, and 6 were assumed to be the maximum rate (either 1000 lbs/yr or the calculated rate based on vapor pressure and tank size) for each HAP. This is an oversimplification which results in greatly exaggerated emission rates. To illustrate the extremely conservative nature of the assumed emission rates, consider that gasoline typically contains no more than 5% benzene; thus, an evaporation rate of at least 20,000 lbs/yr, or about 3300 gallons of gasoline, would be necessary to achieve an emission rate of 1000 lbs/yr of benzene. Simple economics suggest that this would not be a normal condition.

As can be seen from table 2, the NOx emission rate from the 5 MMBtu/hr heater is more than double the nominal insignificant emission rate established in 40 CFR 71. It is nonetheless still quite low at 2.27 tons/yr. Emissions of all other pollutants from all sources are less than the appropriate regulatory insignificant rate of 1 ton/yr or 1000 lbs/yr.

AMBIENT IMPACTS

Source types 1 through 4 are generic source types including a large number of potentially insignificant sources. Maximum likely ambient impacts from these source types were modeled and evaluated against appropriate air quality standards and TLVs.

Ambient impacts from each of the four modeled sources were modeled using EPA's ISCST3 simple & complex terrain model. Modeling parameters included regulatory defaults and a simple terrain polar grid of approximately 100 meter resolution. Each source was modeled for average times of 1, 3, 8, and 24 hours and 1 year. Each source was modeled twice; once with representative meteorological data for the Permian Basin, and again with representative data for the San Juan Basin. The maximum modeled impact for each averaging time was used to evaluate impacts. Table 3 compares maximum modeled ambient impacts of criteria pollutants with National Ambient Air Quality Standards (NAAQS). Table 4 compares modeled 8-hour ambient impacts with the published time weighted average (TWA) and modeled 15 minute impacts with the short term exposure limit (STEL) for the selected HAPs [5].

The typical insignificant activities included in source types 1 and 2 commonly occur near ground level, and, with the exception of the internal combustion sources, occur at or near ambient temperature. Therefore the emission parameters were assumed to be as follows.

Height of release—1 meter
Diameter of release—1 meter
Release temperature—295°K
Vertical velocity—0.1 m/sec

These release parameters are typical of neutrally-buoyant near-ground level sources and are similar to, but more conservative than, the parameters used by EPA in evaluating ambient impacts from 112 (b) HAPs [6]. EPA assumed a 10 meter release height and a nearest receptor distance of 200 meters. The more conservative assumptions used here resulted in higher modeled ambient impacts.

Source types 3 and 4 are heaters. Assumed emission parameters for these sources are typical of small combustion units as follows.

Height of release—3 meters
Diameter of release (type 3-gas fuel)—0.2 meters
(type 4-distillate fuel)—0.076 meters
Release temperature—589°K
Vertical velocity—31.0 m/sec

Stack temperature, diameter, height, and velocity for the 5 MMBtu/hr gas fueled source are typical for small heaters. Stack temperature, velocity, and height for the 1 MMBtu/hr distillate fueled source are the same as for the gas-fueled source, while the diameter is typical of small distillate fueled heaters.

Source type 5, the very large tank, would be a neutrally-buoyant area source, elevated to about 6 meters. Smaller tanks would, of course, be elevated less. Source type 6, the 500 gallon tank, would be a neutrally-buoyant ground-level release. Impacts from sources 5 and 6 were based on modeled impacts from source 2. Thus, predicted impacts from source 5 are higher than if the source were modeled directly. The results are summarized below in tables 4-6.

Table 4
Fraction of NAAQS of Regulated Pollutants

Standard	1	2	3	4	5	6
Annual NOx	0.053		0.026	0.008		
8-hr CO	0.027		5.00e-4	1.46e-4		
1-hr CO	0.030		2.00e-4	4.89e-5		
Annual SO2	0.068		2.00e-4	5.53e-5		
3-hr SO2	0.56		1.00e-4	3.83e-5		
24-hr SO2	0.15		2.00e-4	1.49e-5		
Annual PM-10	0.070		0.004	0.001		
24-hr PM-10	29.40		0.010	5.98e-4		

Table 5
Fraction of 8-hour TWA for Hazardous Air Pollutants

HAP	1	2	3	4	5	6
Benzene		0.003	2.51e-9		0.002	0.001
Ethyl Benzene		2.53e-4			1.41e-4	9.54e-5
Ethylene Glycol						
Formaldehyde						
Hexane		6.24e-4			3.48e-4	2.35e-4
Methanol		4.19e-4			2.34e-4	1.58e-4
Trichloroethlene		4.08e-4			2.28e-4	1.54e-4
Toluene		5.84e-4	3.25e-10		3.26e-4	2.20e-4
Xylenes		2.53e-4	2.27e-11		1.41e-4	9.54e-5

Table 6
Fraction of 15-minute STEL for Hazardous Air Pollutants

HAP	1	2	3	4	5	6
Benzene						
Ethyl Benzene		0.001			6.42e-4	4.34e-4
Ethylene Glycol		0.006			0.003	0.002
Formaldehyde			8.66e-7	2.00e-5		
Hexane						
Methanol		0.002			1.06e-3	7.16e-4
Trichloroethlene		0.001			6.47e-4	4.37e-4
Toluene						
Xylenes		9.56e-4	2.55e-11		5.33e-4	3.60e-4

Formaldehyde impacts from source 2 were not evaluated because sources typically found in this class will not generate formaldehyde at high rates. Short term emission rates from tanks (sources 5 and 6) can often be greater than the annualized average. Benzene impacts are evaluated against the 1995-1996 TWA of 32 mg/m^3. ACGIH has proposed revising this downward to 0.96 mg/m^3.

None of the modeled impacts approach regulatory standards. As a practical matter, 1/100 of the lesser of the TWA or STEL is often considered an appropriate level to protect public health. None of the impacts approach this level.

40 CFR 71 allows up to ten identical insignificant activities each meeting the emissions criteria. Considering that these sources would normally be spaced some distance apart, and that the modeled impacts from a single source decreases greatly at 200 meters and beyond, cumulative impacts from multiple sources are not expected to approach regulatory standards or TLVs.

CONCLUSIONS

Based on this limited study, it appears that the following conclusions may be drawn.

- Many of the insignificant activities identified in the New Mexico insignificant activities list meet the emissions limits of the Federal Operating Permits Program, 40 CFR 71.
- Ambient impacts from the common sources evaluated in this study which meet the Federal limits do not exceed ambient standards, and are well below TLVs.
- Impacts from the only source evaluated here which meets the emission-related criteria in the New Mexico insignificant activities list and does not meet the Federal limits are also well below standards and TLVs.
- Since there is no practical difference between heaters used for domestic heating and gas fueled heaters used for industrial purposes, insignificance could be extended to industrial heaters meeting the same heat rate criteria.

Again, this is a limited study designed to evaluate the realistic emission rates of common insignificant activities and their ambient impacts. While not conclusive, it does indicate that common insignificant activities do not pose a threat to health or to the environment.

REFERENCES

1. "EPA Regulations on Federal Operating Permit Programs," 40 CFR 71, July 1, 1996.

2. New Mexico Environment Department Air Pollution Control Bureau Operating Permit Program, List of Insignificant Activities, September 29, 1995.

3. "EPA Provisions for Chemical Accident Prevention," 40 CFR 68, June 20, 1996.

4. "Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources (AP-42)," US EPA, Office of Air Quality Planning and Standards, Fifth Edition, January 1995.

5. "1995-1996 Threshold Limit Values (TLVs) for Chemical Substances and Physical Agents and Biological Exposure Indices (BEIs)," American Conference of Governmental Industrial Hygienists, 1995.

6. "Documentation of De minimis Emission Rates - Proposed 40 CFR Part 63, Subpart B Background Document," Emission Standards Division, EPA-4531 R\93-035, US EPA Office of Air Quality Planning and Standards, February 1994.

7. Public Law 101-549 (Clean Air Act), Title I, Part A, Sec. 112 (r), November 15, 1990.

8. State of New Mexico, Environment Department, Air Quality Regulations, New Mexico Administrative Code Title 20, Chapter 2, Part 70, November 30, 1995.

Emerging Technologies with Petroleum Environmental Applications

INVESTIGATION OF THE STRENGTH OF ORGANIC POLLUTANT ADSORPTION TO MINERAL SURFACES

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A preliminary investigation was conducted on the suitability of the dynamic Wilhelmy plate technique for examining the adsorption of different classes of organic pollutant molecules to the surfaces of mineral thin sections. Plates (thin sections) made both from marble and from quartzite were examined and 1,4-dinitrobenzene represented the first class of pollutant studied: nitroaromatics. Plates of each mineral type were completely immersed in toluene solutions of 1,4-dinitrobenzene for varying periods of time before they were passed into and out of aqueous phases during the Wilhelmy experiments. Magnitudes and changes in adhesion tensions were used to evaluate the strength and persistence of adsorption.

INTRODUCTION

Sorption from aqueous solution to solid surfaces is one of the key processes determining the distribution and fate of organic pollutants in the environment.

This paper reports on investigation of the suitability of the dynamic Wilhelmy plate technique for measuring the strength of interaction between organic pollutant molecules and mineral surfaces. The Wilhelmy technique involves raising an oil/aqueous phase mixture until it comes into contact with a rock plate (having dimensions approximating those of a microscope slide) that has been suspended from a microbalance. When the plate passes through the oil/water interface, the force on the plate is equal to the adhesion tension. Adhesion tension has been used as a quantitative measure of wettability in oil/brine/rock systems.[1] Details concerning use of the dynamic Wilhelmy plate technique and its applicability to solid-fluid interactions are described by Andersen, et al.(1)

Adsorption of oleic acid to a glass plate has been studied using the Wilhelmy technique by dissolving the oleic acid in the hexadecane layer of a hexadecane-water mixture (1). In another study, Haderlein and Schwarzenbach have found that solution pH and the type of cation adsorbed to a siloxane surface influences the strength with which nitroaromatic compounds (NACs) adsorb to homoionic kaolinite (2). NACs are widely used as explosives, in the synthesis of pesticides and dyes, as solvents, and as herbicides and insecticides.

We report work done with one of the same NACs investigated by Haderlein and Schwarzenbach: 2,4-Dinitrobenzene (2,4-DNB). Showing that the Wilhelmy technique can be used for organic pollutant/mineral adsorption would be very significant because it is a much simpler and faster way to obtain data than the method used by Haderlein and Schwarzenbach. The Wilhelmy technique is also ideal for obtaining data that are difficult and/or impossible to get by other methods. For example, aqueous solutions in which the pH and ionic composition are systematically varied would allow construction of novel three-dimensional plots of adhesion tension as a function of pH and cation concentration, as recently described for the first time using oil/brine/rock systems (3). Positive results from this feasibility study could lead to an expanded project involving other classes of organic pollutant molecules, minerals with varying composition, effects of water flow velocity, etc.

EXPERIMENTAL

During a dynamic Wilhelmy test a plate hanging from a wire connected to a microbalance is slowly (0.127 mm/s), and in a continuous motion, immersed in, then removed from, an immiscible layer of an organic liquid on water. A computer interfaced stepper motor controls the motion of

a vessel containing the liquid mixture. As the plate travels through the liquid layers the force on the plate changes and affects the weight readings of the microbalance. The computer automatically converts the microbalance readings to adhesion tensions. Figure 1 is a schematic of the dynamic Wilhelmy apparatus.

The organic phase consisted of pure toluene or a 0.1 *M* solution of 2,4-DNB in toluene. The solid phase consisted of marble and quartzite plates approximately 2 cm x 2 cm and 2 mm thickness. Each type of plate was completely submerged in one of the organic phases for varying lengths of time (minimum of 1 day), then immersed into and removed from the water layer below it.

RESULTS

Figures 2 and 3 show Wilhelmy plots obtained with 100% fused quartz plates containing markedly different surfaces as they passed through a mixture of dodecane on water (4). These figures simulate the types of plots obtained with a mineral substrate in the absence and presence of an organic phase adhering to its surface. The plot in Fig. 2 was produced by a quartz plate with a naturally water-wetting (hydrophilic) surface. When the plate entered the water layer, a large increase in adhesion tension occurred as the water strongly adhered to the plate's surface. The plate used in the test that produced the plot shown in Fig. 3 had its surface chemically modified by a silylating agent. The silane produced a hydrophobic surface that was not wetted by water. Consequently a dramatic decrease in adhesion tension occurred when this plate entered the water layer.

In the work reported in this paper plates consisting of actual mineral thin sections were completely immersed in the organic phase for a minimum of 1 day. This amount of time was needed for the 2,4-DNB to at least physically adsorb to the surface of the mineral at ambient temperature.

Figures 4 and 5, respectively, show that a pure toluene phase adhered weakly to the surfaces of both marble and quartzite and was easily replaced by water. Adhesion was stronger on the marble surface.

2,4-DNB remained strongly adhered to the marble surface after a submersion period of 10 days (Figure 6). 2,4-DNB adhered less strongly to the quartzite surface and was at least partially displaced by water after the plate traveled through the aqueous layer (Figure 7)

Plots of adhesion cycles were reproducible for both types of plates investigated.

CONCLUSIONS

The dynamic Wilhelmy apparatus was successfully used to qualitatively evaluate the strength of interaction between 2,4-DNB and mineral surfaces consisting of marble and quartzite

Our experiments demonstrate the potential for integration of adhesion tension data in mechanistic models describing the distribution and fate of organic pollutants in the environment.

REFERENCES CITED

1. Andersen, M.A., Thomas, D.C., and Teeters, D.C., "A New Formation Wettability Test: The Dynamic Wilhelmy Plate Wettability Technique," Paper No. 17368, *SPE/DOE Enhanced Oil Recovery Symposium*, 529-538 (1988).

2. Haderlein, S.B., and Schearzenback, R.P., "Adsorption of Substituted Nitrobenzenes and Nitrophenols to Mineral Surfaces,"*Environ. Sci. Technol. 27*, 316-326 (1993).

3. D. Teeters, N.E. Takach, and W.A. Redman, "Aerobic and Anaerobic Three Dimensional Wetting Maps for Oil/Brine/Solid Systems," in proceedings of the *6th IFP Research Conference on Exploration-Production: Physical Chemistry of Colloids and Interfaces in Oil Production*, St. Raphaël, France, 47-52 (1991).

4. Takach, N.E., "Vapor Phase Reactions of Organoaminosilanes with Quartz,"*J. Colloid Interface Sci. 162*, 496-502 (1994).

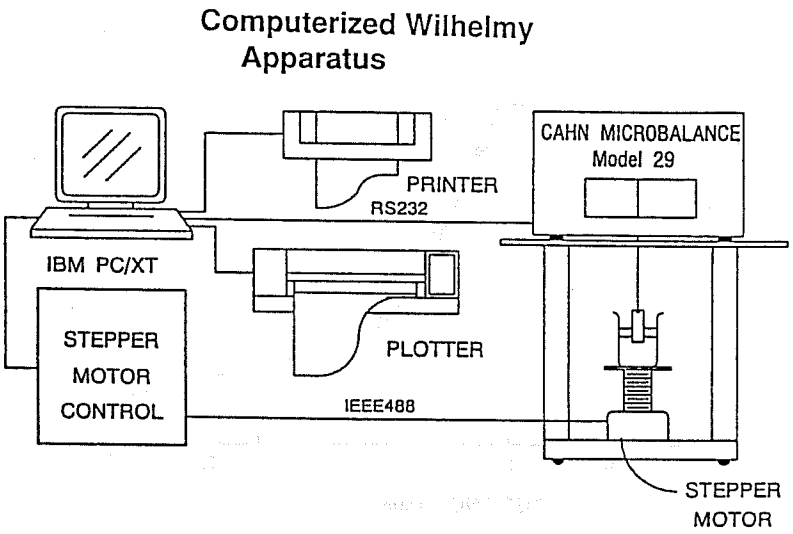

Figure 1. Schematic of the computerized dynamic Wilhelmy plate apparatus.

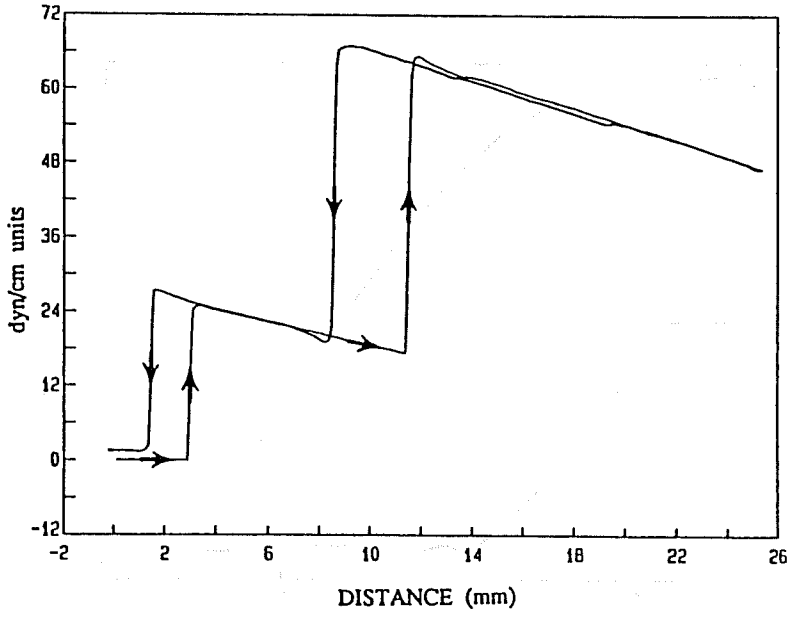

Figure 2. Nearly ideal water-wetting plot produced during a Wilhelmy test on an unsilylated quartz plate.

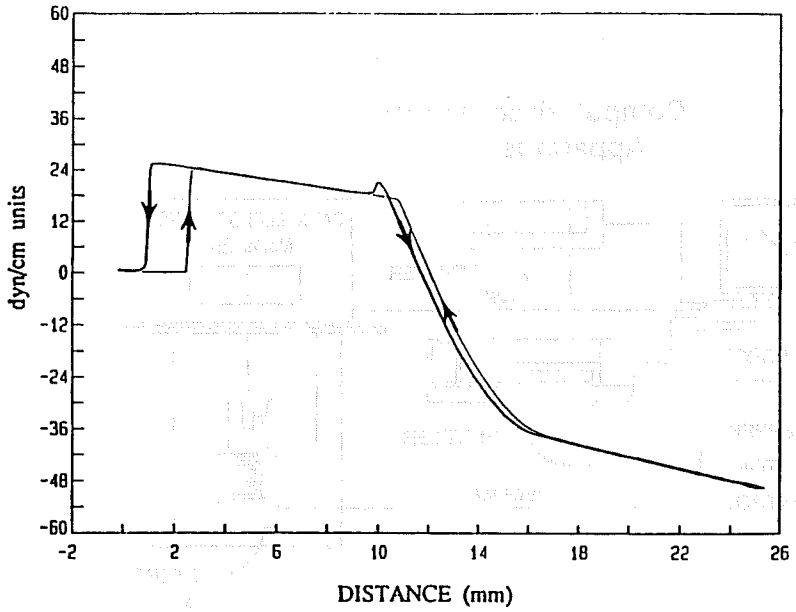

Figure 3. Quartz plate after silylation with hexamethyldisilazane at 275°C. The strong drop in adhesion tension as the plate advanced through the water layer (starting at approximately 10 mm on the horizontal scale), smooth lines, and essentially zero hysteresis throughout, are consistent with a nearly ideal oil-wetting plot.

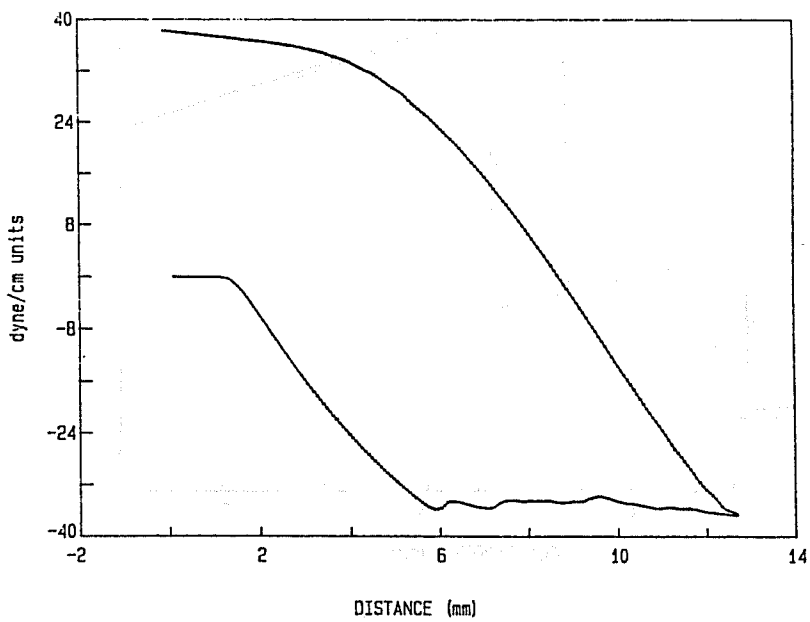

Figure 4. Wilhelmy plot of system involving a marble plate submerged in pure toluene, then immersed into and removed from water. A decrease in adhesion tension in the aqueous layer (distance between approximately 2 cm and 12 cm) corresponds to adsorption of a hydrophobic phase to the mineral surface.

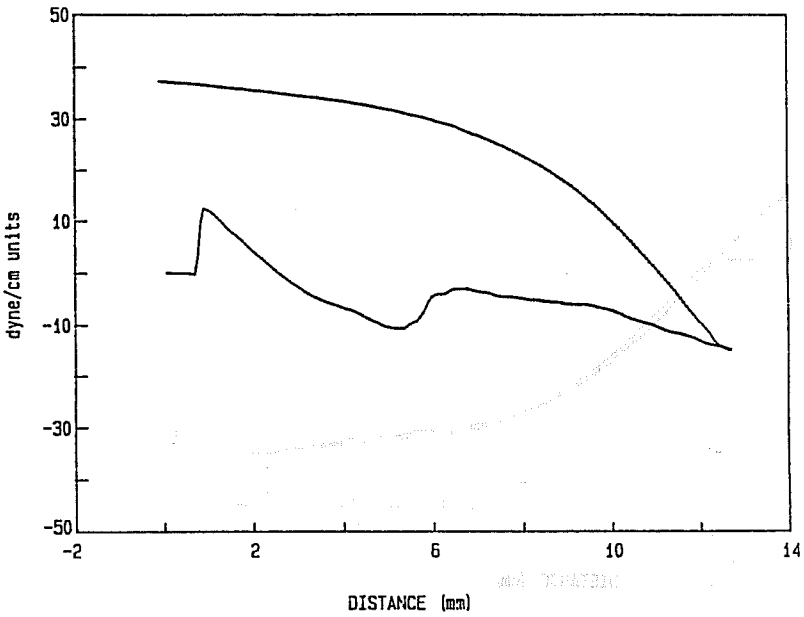

Figure 5. Wilhelmy plot of system involving quartzite plate submerged in pure toluene, then immersed into and removed from water.

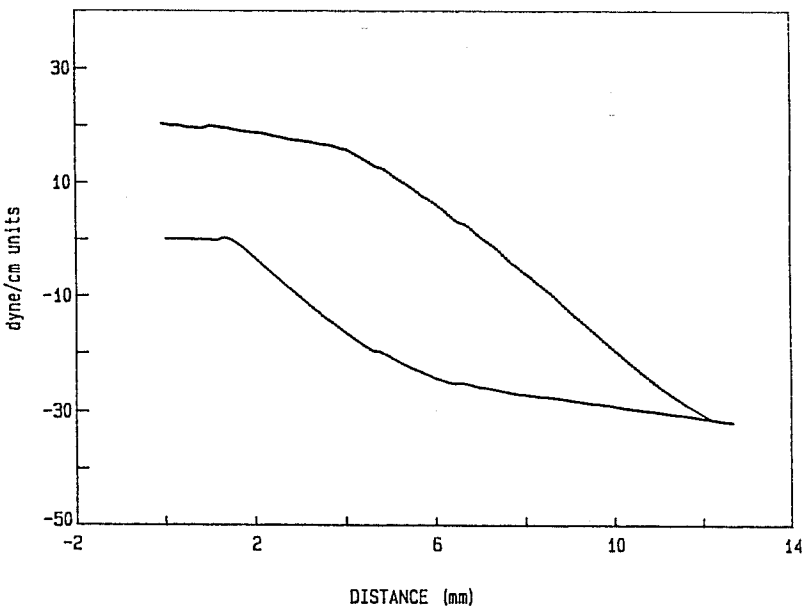

Figure 6. Wilhelmy plot of system involving marble plate submerged in a 2,4-DNB/toluene solution, then immersed into and removed from water.

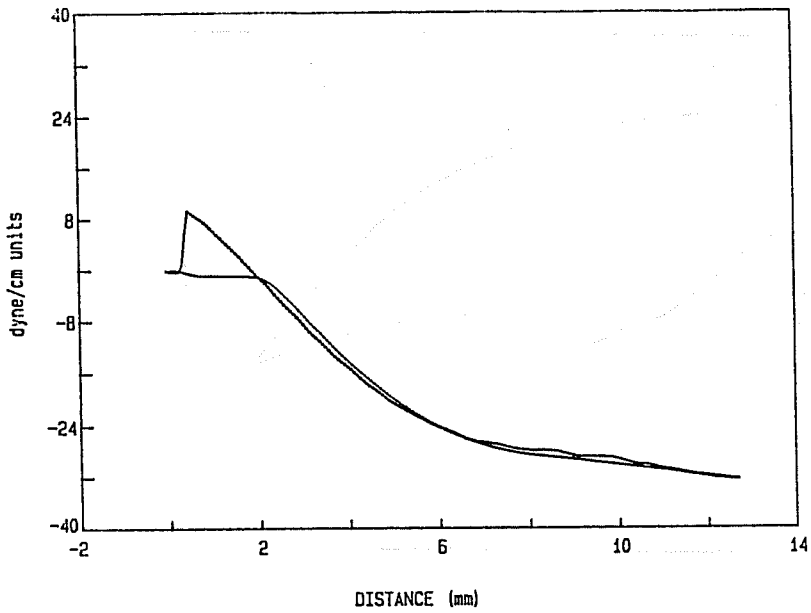

Figure 7. Wilhelmy plot of system involving quartzite plate submerged in a 2,4-DNB/toluene solution, then immersed into and removed from water.

Microbially Gelled Biopolymer Improves Conformance Control in Layered Porous Media

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ABSTRACT

Pump-and-treat operations are often ineffective at removing contaminants from the subsurface because residual contaminants remain in isolated regions of the aquifer after the zones of high permeability are "swept" of the majority of the target material. Aquifer heterogeneity causes nonuniform mobility of the drive fluid, which leads to fingering and flow bypass of contaminant-containing low-permeability regions. This often occurs with dense solvents, which sink to the bottom of the aquifer and accumulate in low-permeability regions. Remediation of hydrocarbon-contaminated aquifers has the same goal as oil production – removal of specific hydrocarbons from the pore space of saturated porous media. Gelled polymers are commonly used in oil production to modify permeability of porous media and improve sweep efficiency of the drive fluid. To achieve in depth permeability modification, gelled polymers must be injected into porous media in a low-viscosity, pregel form and caused to form a gel in situ. The gel must also be a non-toxic compound to be useful for aquifer applications. Curdlan, an extracellular ß-1,3-glucan polymer produced by the soil bacterium *Alcaligenes faecalis* var. *myxogenes*, exhibits a pH-dependent gelation, being soluble in alkaline solutions above pH 10.0 and forming a gel below pH 9.5. This presentation describes a process using alkaliphilic bacteria to cause gelation of alkaline-soluble curdlan biopolymer. Curdlan biopolymer was mixed with microbial nutrients and inoculated with alkaliphilic isolates. The pregel polymer solution had a viscosity of 8.0 cp at pH 11.5. The rate of gel formation could be controlled by adjusting the inoculum. Pregel polymer was injected into Berea sandstone cores and incubated 7 days. Permeability of the cores was decreased from 852 mD to 2.99 mD and 904 mD to 4.86 mD, respectively, giving residual resistance factors of 334 and 186. Microbially gelled polymer was effective at diverting fluid flow from high-permeability regions of porous media to low-permeability zones.

INTRODUCTION

Petroleum products released into soil or groundwater often pose unacceptable risk to public health or environmental quality and require remedial activity. There are several remediation methods that can be employed, depending on the nature and volume of contaminant, site-specific conditions, and the target level of cleanup desired. Recovery techniques, such as pump-and-treat, are used in the majority of remediation programs and are most effective when free product is present. In pump-and-treat operations, water is caused to circulate through the subsurface from a point of injection to extraction wells. In this case, water is used as a drive fluid to push hydrocarbons through the subsurface to extraction wells where they can be removed. The efficiency of pump-and-treat operations is ultimately determined by how effective the water is at pushing the contaminants to the extraction wells.

Pump-and-treat operations are often ineffective in removing hydrocarbons from the subsurface (1). The rate of recovery of contaminants from recovery wells is initially high as bulk phase contaminants are removed; however, as the remediation program continues the rate of recovery decreases and commonly levels off at some concentration above the regulatory limit. This phenomenon, referred to as tailing, greatly increases the amount of time necessary to remediate a site and may ultimately determine if the target level of cleanup can be achieved.

Tailing occurs because hydrocarbons become trapped as non-aqueous phase liquids (NAPLs) in the subsurface matrix and serve as a source for continuous dissolution of contamination. Hydrocarbons can exist as a bulk phase and/or remain in significant quantities as residual saturation after the bulk phase has been removed (2). In addition, aquifer heterogeneity causes nonuniform mobility of the drive fluid, which leads to fingering and flow bypass of contaminant-containing low-permeability regions. This problem is compounded by residual saturation of the hydrocarbon, which increases as grain size and permeability decreases (2). Residual saturation further lowers the relative permeability of the contaminated zone to the aqueous drive phase causing isolation of the contaminant-containing zone from the ongoing treatment. This commonly occurs with dense chlorinated solvents, which sink through the water table and accumulate in low-permeability regions of aquifers.

Among the most persistent environmental contaminants found in groundwater are the chlorinated solvents, particularly trichloroethylene (TCE) and tetrachloroethylene (PCE). All Department of Energy sites and nearly 80% of Superfund sites are contaminated in part by these chlorinated compounds (3). In addition to being widespread environmental pollutants, these solvents are problematic to remediate. TCE and PCE are more dense than water and consequently sink through the water table and accumulate as dense NAPLs (DNAPLs) in low-permeability regions at the bottom of groundwater aquifers. DNAPLs are difficult to mobilize using traditional pump-and-treat methods

because they persist in a region of the aquifer that may not be reached by the drive fluid. Also contributing to their recalcitrant nature, TCE and PCE are resistant to bioremediation. Degradation studies have failed to show biodegradation of a suite of chlorinated aliphatic solvents under aerobic aquifer conditions (4). Innovative products and methods are needed to improve the efficacy of groundwater remediation technology for these common contaminants.

Oil production and remediation of contaminated aquifers have the same goal – removal of specific compounds from the pore space of saturated porous media. For extraction systems, such as pump-and-treat or primary oil recovery, the efficiency of the system decreases over time. During initial pumping, the zones of higher permeability, such as sand and gravel layers, are "swept" of the vast majority of the target material residing in the pore space. Remaining is the target material, which is chemically sorbed to the media, trapped by capillary attraction, isolated within a pore that is poorly connected to the flowpath, or trapped in fine-grained portions of the porous media by any of the above mechanisms (5).

Gelled polymers are commonly used in oil production to modify permeability of porous media and improve sweep efficiency of the drive fluid (6). By reducing the permeability, gelled polymers are able to physically block fluid flow through these highly permeable zones. Sealing these high-permeability zones from the ensuing waterflood reduces channeling of the injection fluid and diverts it into previously bypassed low-permeability regions, increasing the sweep efficiency (7). To achieve in depth permeability modification, gelled polymers must be injected into porous media as a low-viscosity fluid and caused to form a gel in situ. Therefore, the polymer must be gelled by some delayed triggering reaction. The gel must also be a non-toxic compound to be useful for aquifer applications.

Curdlan biopolymer is an extracellular ß-1,3-glucan produced by the soil bacterium *Alcaligenes faecalis* var. *myxogenes*. It is non-toxic with no human nutritional value and was originally developed as a low calorie food additive (8). Similar "curdlan-type" glucan biopolymers have been described from *Agrobacterium* (9) and *Cellulomonas* (10). Curdlan-type polymers are attractive for permeability modification because they exhibits a pH-dependent transition between a gel and a soluble state. In alkaline solutions of pH greater than ca. 10, curdlan is soluble and can be mixed as a low viscosity gelant. In solutions below ca. pH 9 curdlan forms an insoluble gel. Gelled curdlan is stable in neutral or acidic solutions to pH 2 and insoluble to most organic solvents.

Microbial technologies have been successfully used in the petroleum industry to improve recovery of oil from porous media (11). These same techniques can be applied to the environmental industry to improve performance of aquifer remediation technology. In addition to being technically successful, microbial processes are environmentally friendly and suitable for groundwater

aquifer applications. This paper will discuss a novel microbially gelled polymer process that is able to modify the permeability of porous media. This process can be used to form biocontainment barriers to minimize and define treatment zones. It can also selectively plug high-permeability zones, causing a diversion of drive fluid into previously isolated contaminant containing regions and improved product recovery in pump-and-treat operations.

MATERIALS AND METHODS

Bacteria

Alkaliphilic bacteria used in this study were enriched from lake sediments collected in a dry lake bed near Zzyzx, California. All samples were cultured anaerobically in N_2-purged Hungate tubes on Trypticase Soy Broth (TSB) adjusted to pH 11.5 and 5% NaCl. Isolates SL-1A and SL-2A were picked from streak plates of the alkaliphilic consortia. Strain SL-1A is a gram-positive facultative diplococci. Strain SL-2A is an anaerobic, spore-forming bacillus which stains gram-variable. Both strains have complex nutrient requirements. The isolated strains grow anaerobically in TSB with an initial pH 11.5 and lower the pH of the medium to near 7.

Gelation Tests

Bottle tests were conducted to determine if alkaliphilic microorganisms can cause gelation of alkaline-solubilized curdlan biopolymer. Polymer gelant solution was prepared by dissolving 0.5% curdlan into 1N KOH and adding per 100 ml: Na_2CO_3, 0.225 g; TSB, 3.0 g; NaCl, 3.0 g; pH was adjusted to 11.5 with concentrated KOH. Polymer gelant was aliquoted into Hungate tubes, purged with N_2 and inoculated with undefined alkaliphilic consortia; no pure strains were tested. All bottle tests were conducted at 25°C. Bottle tests were monitored for up to six months to assess the stability of the polymer system.

Permeability Modification

The ability of the microbially gelled polymer system to modify permeability of porous media was measured in coreflood experiments. Berea sandstone cores, ca. 1.5 in. diameter by 10 in. length, were evacuated two hours and saturated with degassed 0.5% NaCl. After loading cores into coreholders, 2 pore volumes (PV) 0.5% NaCl was pumped through each core at 2.0 ml/min. Permeability of each core was measured before treatment with 0.5% NaCl. Cores were preflushed with 2 PV thymolphthalein-tagged 0.02 M $CO_3^=$ buffer at pH

11.5 to stabilize core pH prior to polymer injection. Polymer gelant solution was prepared as for the bottle tests plus 1% glucose. Polymer gelant solution was inoculated with 1.0 ml each SL-1A and SL-2A from stationary phase cultures. One PV inoculated polymer gelant was injected into each core at 2.5 ml/min. After polymer injection, cores were shut in for 7 days and incubated at 27°C. Samples of polymer gelant were collected in Hungate tubes concurrent with the injection and incubated with the core. Polymer gelation in accompanying Hungate tubes were monitored during the incubation period. After the incubation period, flow was established through each core with 1 PV 0.5% NaCl prior to measurement of post-treatment permeability. Core effluent pH was monitored during preflush and polymer injection, and after treatment to assess pH modification by the bacteria.

RESULTS

Gelation Tests

Firm gel formed in all polymer gelant solutions within 2 - 4 days after inoculation with alkaliphilic consortia. The gelled polymer had a pH of approximately 8.8 - 9.0 when measured the first day after gelation, suggesting that gelation had occurred near pH 9.0. The pH of polymer gel samples continued to decrease to near neutral pH of 7.0 - 7.5. Gel forming in all inoculated samples remained firm for 6 months. Gelation did not occur in an uninoculated control sample during the same 6 month period.

Permeability Modification

Core pH stabilized at 11.4 - 11.5 after displacement of approximately 1.5 PV (Figure 1). All inoculated polymer samples accompanying core C-01 gelled after 2 days of incubation. Gelation of polymer samples accompanying core C-02 occurred more slowly with gelation times of 5 - 12 days. An uninoculated control polymer sample did not form a gel after 2 months incubation. After incubation, core effluent pH was measured to assess pH modification by the microbial trigger. Cores had an initial pH of 11.4 - 11.5 at the time they were shut in. Effluent from the cores was decreased to pH 7 - 8.4 after microbial treatment (Figure 2).

Permeability is the capacity of a porous media to facilitate fluid flow under the influence of a pressure gradient. It is determined by the porosity (void volume) and how the pore spaces are interconnected. The measured unit of permeability is the darcy (D), which is described by Darcy's Law (1):

$$k = \frac{q\mu L}{A\Delta P} \quad (1)$$

where:

k = permeability (D, darcies)
μ = fluid viscosity (cp, centipoise)
A = cross sectional area (cm^2)
q = fluid flow rate (ml/s)
L = length of flow path (cm)
ΔP = pressure drop across L (atm)

Residual Resistance Factor, F_{RR}, is a measure of how well the polymer maintains form as it flows through porous media and is calculated by the equation (2):

$$F_{RR} = \frac{\left\{\frac{Q}{\Delta P}\right\}_{\text{before treatment}}}{\left\{\frac{Q}{\Delta P}\right\}_{\text{after treatment}}} \quad (2)$$

where Q and ΔP are steady-state effluent rates and pressure drop across the core, respectively. Permeability of the cores was decreased from 852 and 904 mD initial permeability to 2.99 and 4.86 mD, respectively, after treatment (Table 1). When F_{RR} are plotted against frontal velocity, Figure 3 shows that gelled curdlan exhibits slight shear thinning, typical for a gelled polymer. Nonetheless, F_{RR} range from near 150 to 300 at frontal velocity up to 5 ft/day. The gelled polymer in Hungate tubes accompanying core injections remained firm for 1 - 2 months and then became soluble. A solubilized polymer sample was viewed by microscopy and found to have microbial growth.

SUMMARY

Microbially gelled curdlan biopolymer effectively modified the permeability of porous media in coreflood experiments. Permeability of Berea sandstone cores was decreased by more than 99% after treatment with 0.5% microbially gelled polymer. Curdlan-type polymers can be mixed in alkaline solutions as low viscosity gelants which can be injected deeply into porous media. Specially isolated alkaliphilic bacteria are able to withstand the strong alkaline conditions necessary to solubilize curdlan and produce acids in situ to lower the pH of the polymer gelant solution. After injection and placement of the gelant, the microbially driven pH shift causes it to form a rigid gel.

Pump-and-treat remediation technologies can be improved by controlling flow patterns within the aquifer. As fluid migrates through porous media it follows the path of least resistance – the high-permeability zones. Contaminant-containing low-permeability regions can be bypassed by injection fluids and become isolated sources of continuous contamination. Gelled polymers are able to

lower the permeability and physically block fluid flow through high-permeability zones. Blocking these channels diverts injection fluids into previously isolated lower-permeability regions. Conformance control therefore improves remediation efficiency by reducing channeling of injection fluids and increasing flow into low-permeability regions. The microbially gelled biopolymer system is suitable for groundwater aquifer applications. Curdlan is a non-toxic food grade biopolymer. Microbial metabolism provides a simple, yet effective, mechanism to cause delayed gelation of the polymer and provide effective conformance control.

ACKNOWLEGMENT

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REFERENCES

1. Imhoff, P. T., Gleyzer, S. N., McBride, J. F., Vancho, L. A., Okuda, I., and Miller, C. T., "Cosolvent-enhanced remediation of residual dense nonaqueous phase liquids: experimental investigation," *Environ. Sci. Technol.* 29, 1966-1976 (1995) August.

2. Testa, S. M., and Winegardner, D. L., *Restoration of petroleum-contaminated aquifers*, Chelsea, MI: Lewis Publishers, 1991.

3. Shannon, D., "Bioremediation consortium to tackle chlorinated solvents," *Environ. Sci. Technol.* 29, 402A (1995) September.

4. Nielsen, P. H., Bjerg, P. L., Nielsen, P., Smith, P., and Christensen, T. H. "In situ and laboratory determined first-order degradation rate constants of specific organic compounds in an aerobic aquifer," *Environ. Sci. Technol.* 30, 31-37 (1996) January.

5. Bryant, R. S., Burchfield, T. E., Chase, K. L., Bertus, K. M., and Stepp, A. K., "Optimization of microbial formulations for oil recovery: mechanisms of oil mobilization, transport of microbes and metabolites, and effects of additive," presented at the 64th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, SPE Paper 19686, San Antonio, TX, October 8-11, 1989.

6. Borling, D., Chan, K., Hughes, T., and Sydansk, R., "Pushing out the oil with conformance control," *Oilfield Rev.* 6, 44-58 (1994).

7. Gao, H. W., and Burchfield, T. E., "The effects of layer permeability contrast and crossflow on the effectiveness of polymer gel treatments in polymer floods and waterfloods," presented at the Society of Petroleum Engineers Production Operation Symposium, SPE paper 25453, Oklahoma City, OK, March 21-23, 1993.

8. Harada, T., "Production, properties, and application of curdlan," 265-283 in *Extracellular microbial polysaccharides*, Sandford, P. A., and Laskin, A., ed. Washington: American Chemical Society, 1977.

9. Nakanishi, I., Kimura, K., Suzuki, T., Ishikawa, M., Banno, I., Sakane, T., and Harada, T., "Demonstration of curdlan-type polysaccharide and some other ß-1,3-glucan in microorganisms with aniline blue," *J. Gen. Appl. Microbiol.* 22, 1-11 (1976).

10. Buller, C. S., and Voepel, K. C., "Production and purification of an extracellular polyglucan produced by *Cellulomonas flavigena* strain KU," *J. Ind. Microbiol.* 5, 139-146 (1990).

11. Bryant, R. S., and Burchfield, T. E., "Review of Microbial Technology for Improving Oil Recovery," SPE Res. Eng., 151-154 (1989) May.

Table 1. Permeability modification in Berea sandstone cores by microbially gelled 0.5% curdlan biopolymer

Berea core	Initial permeability (mD)	Permeability after treatment (mD)
C-01	852	2.99
C-02	904	4.86

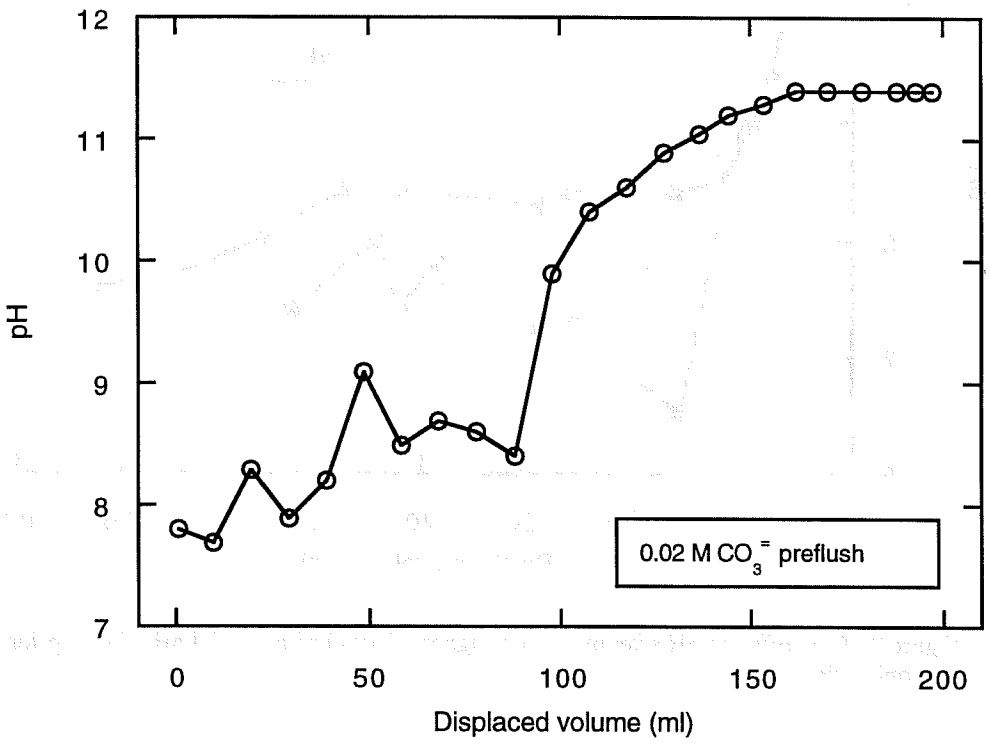

Figure 1. Core C-01 effluent during preflush and polymer injection. Core was preflushed with 2 PV 0.02 M $CO_3^{=}$ buffer prior to injection of 1 PV pregelled polymer.

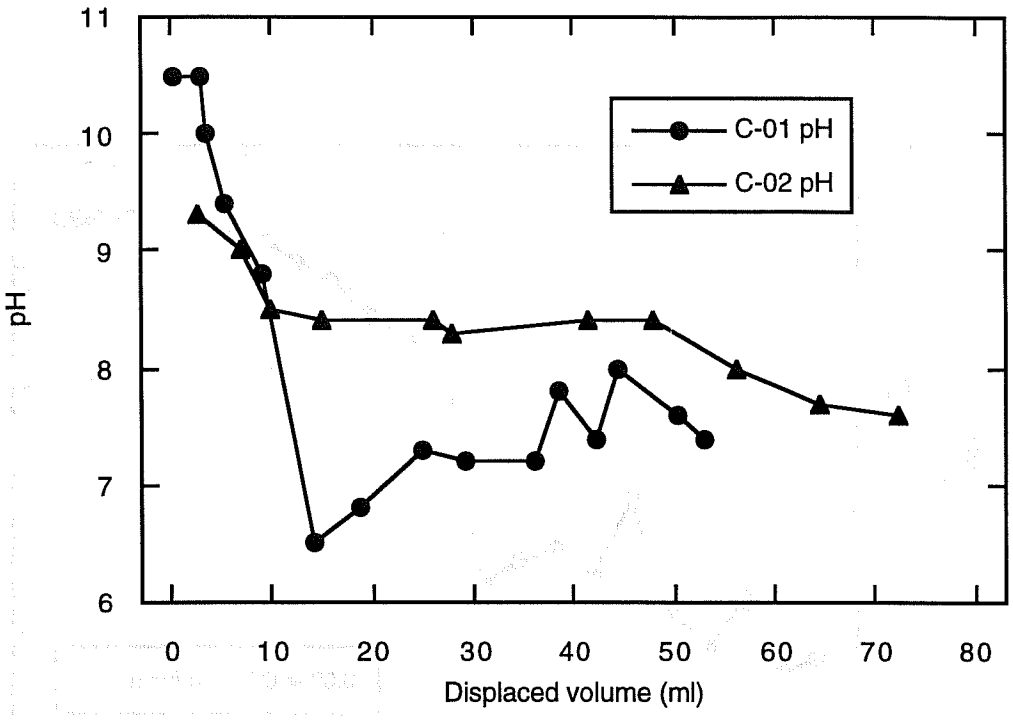

Figure 2. Core effluent pH after microbial trigger. Cores had an initial pH of 11.4 prior to microbial trigger.

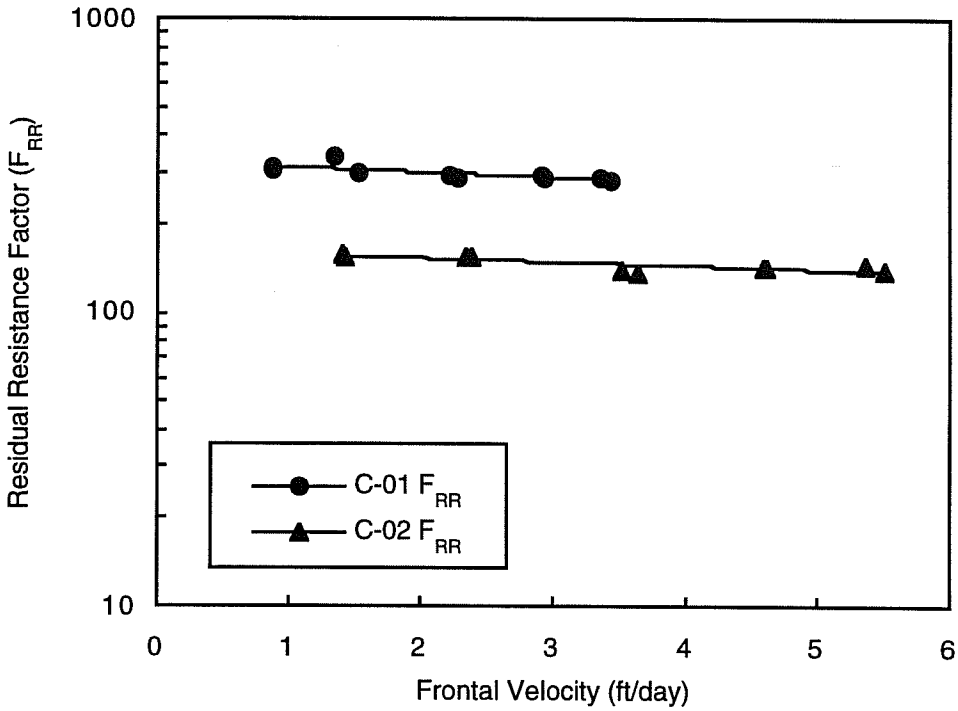

Figure 3. Permeability modification in Berea sandstone cores after treatment with microbially gelled 0.5% curdlan biopolymer.

Clays: Environmental Solutions and Dilemmas

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Abstract

Environmental pollutants from industrial processes continue to be problematic; aromatic compounds, PAH's, and even metals from industrial extractions are major concerns. Containment, adsorption, and concentration methods are designed for dealing with the pollutants and they utilize sorbent materials such as activated carbon and synthetic liners. Sorbent or sealant materials should be readily available, cost-effective, and have large capacities for selective interactions. Clays can compete favorably if not surpass the performance and requirements of other sorbents. So why aren't they used to an even greater extent? The dilemma is that clays have their own unique drawbacks. First, if clay is used in bulk form as the major constituent of soil, then particle size, type of clay, and chemical interferences of the other components become important parameters as they will affect the adsorption interaction. In other environmental situations the method of choice would need to incorporate materials with hydraulic properties. Moisture, available cations, plus the type of clay will affect the hydraulic properties that are crucial for the specific environmental application. Another notorious problem for clay liners is that the hydration-dehydration cycle of the clays causes irreversible cracking that renders the clay barrier useless. However, because clays are complex chemical reagents they are capable of many varied interactions. By using this chemistry one can affect all the properties that were addressed above to improve their very specific utility and overcome the drawbacks.

INTRODUCTION

Pollutants in the air, water, and soil continue to be problematic. There is a definite need to extract, sorb, concentrate, contain, or encapsulate these pollutants. Natural and synthetic materials are used for these purposes and clays also play a major role. There are inherent problems with most sorbents, including clays. Clays are used for several reasons. They are abundant and relatively accessible in most parts of the world. Consequently, clays are also inexpensive. In addition, they in themselves are non-toxic, and due to their physical characteristics they have high capacities for adsorption. A comparison of clays to other sorbents will demonstrate their potential application as environmental sorbents and the increase in their demand. The comparison will begin by noting the attributes of non-clay materials first; the clay discussion will follow.

NON-CLAY SORBENTS

Synthetic materials such as polymers and resins are designed to be selective adsorbents but they are not available in bulk quantities and are often too expensive for large scale applications. Geotextiles and large plastic sheets, for example, are used as liners for pond containment but problems stem from poor sealing of the liner sections and from liner degradation resulting from fluctuations in temperature and exposure to certain chemicals. Graphite is another sorbent that is used extensively and it can be produced by controlled combustion of organic materials. The fundamental mechanism of adsorption for graphite is specific; non-dispersive bonding to graphite involves π-π interactions. This condition limits the types of compounds or pollutants that can be sorbed by graphite. The results in Table 1 show that the aromatic compound, benzene, interacts strongly via π-π interactions with graphite but the alkane, n-hexane, with the same number of carbons exhibits a weaker adsorption (1). Silica and alumina are also used but the binding energies to these materials are small; some hydrogen bonding is possible. However, the binding is non-selective, yet selectivity is a quality that is necessary for trace pollutant adsorption.

CLAY SORBENTS

For the comparison, clay materials are used because they have qualities or the potential to bind pollutants as effectively as non-clay materials. Clays are natural polymeric materials that are also ion-exchangers. With appropriate modifications they can serve many of the same functions of the synthetic polymers. The clay materials however, can be used in both aqueous and organic solvents and they withstand acid-base variations from pH4 to pH14. Redox reagents such as dithionite and peroxide do not affect the base clay material. The clay materials themselves also withstand 250-300 °C temperatures before dehydroxylation begins to occur (2). Clays are fine particulates, less than 2 μm, that can be applied uniformly in dry form or as a slurry; this quality is important for large scale applications of liners. There isn't just one mechanism for binding to clays; instead there are several and that is the advantage of using clays. Ion-exchange has already been mentioned and this mechanism provides a means of selectively binding metals because the binding strengths vary according to the lyotropic series, i.e. the charge density of the hydrated metal (3). Ion-exchange also occurs readily with organic cations. In this fashion the modified clays can now act as surfactants or the adsorbing surface changed from a hydrophilic to a hydrophobic, organic partitioning surface. Most recently, a mechanism that is becoming very important is due to the fact that clays can be porous and now even designed to have pores of pre-determined size and shape (4,5,6). The energies of adsorption for porous clays increase several-fold with respect to the non-porous materials if the shape and size of the pore closely match those of the adsorbate (7). Selective adsorption by this mechanism is necessary for removal of trace pollutants in complex matrices. Because the clay platelets are themselves charged, the proposed mechanisms of adsorption involve ion-induced dipole interactions (8,9). The energies of adsorption for these interactions are substantial and for aromatic compounds the energies are comparable to the adsorption energies on graphite, see Table 1. Note that the energy of adsorption of hexane on the sodium clay is small, but the adsorption can be completely altered by designing a completely different modified clay; this is verified by noting the very escalated energy of adsorption of pentane, hexane would be even larger because it has one more carbon. An

added advantage is that clays can be used for air as well as for water environments.

THE DILEMMA

Clays have just been portrayed as exceptional adsorbents. Yet clays are not always used to solve environmental problems. The dilemma of whether to use a clay or some other sorbent stems from the fact that sorbents and clays all have drawbacks. The first major disadvantage of clays is that the reversibility of the binding process cannot be achieved or controlled, and is poorly understood. The second disadvantage for environmental applications is that clays swell in aqueous environments. These aspects need to be discussed in more detail.

The first situation, that of strong binding and questionable desorption, occurs for both organic and inorganic compounds. For the organic compounds, clays have large capacities as well as large binding energies, large enough for all compounds that the selectivity element is lost. This situation becomes a disadvantage if what is needed is the removal of a trace pollutant and the sorbent becomes saturated with competing compounds that are not a threat. The strength of the binding energy poses a second problem: the pollutants are contained but what to do with this enhanced pollutant-clay mass? One favorable point though, is that solid phase extraction with clays is preferred to liquid extraction methods that involve liquid phases that could be just as detrimental as the pollutant itself.

Measured binding energies are large, but they are exclusively for adsorbate-clay interactions. Adsorbed water will alter the adsorption energies. In an aqueous environment the solvent could compete favorably with the clay material for the pollutant. This is the problem with pollutant leaching. As shown in Figure 1, waste management facilities incorporate soils for the permeable layer and the top liner is often a porous geotextile that has clay adhered to its surface. The function of the clay in both cases is to sorb chemicals that seep through the landfill while allowing water to continue percolating to the drains. The binding of the pollutants to the clays can be altered by water, pH, and competing compounds. Thus,

understanding desorption and the associated energies becomes important. The migration rate of petroleum constituents in soils is attenuated by the clay component in the soil. However, the net adsorption energies are again affected by water, pH, and other competing compounds.

Metal binding to clays is another environmental concern. Clays bind the different metals and the binding strengths vary with the charge density of the metal. The hydrated sphere of the ion becomes the governing parameter. Competitive binding and adsorption are important aspects to leaching and contamination of aquifers. These mechanisms as well as the effects of the matrix pH and ion concentrations are not well understood. An example of an environmental problem that is a result of clay desorption processes is that of cesium in the soil at nuclear facilities and areas such as the Hanford site (10-14). At this time the radioactive Cs cannot be desorbed from the soil to concentrate it for proper disposal. Cesium is irreversibly bound to the soil and this is an urgent remediation problem.

The second drawback of clays is that they swell when exposed to moisture. The reverse process, desiccation, also presents its own unique set of problems to environmental remediation. Because clays swell, they cannot be contained in a column to remove pollutants from an aqueous stream. Columns must have porous retainers such as fritted disks at the exits of the column to contain the sorbent, but the swelling of the clays plugs the retainer pores. For this reason, there has been a shift to zeolites and the tremendous adsorption capacities and selectivity of the layered clays is not being utilized. For landfills the opposite action is the problem, see Figure 1. The clay liners are compacted and moisture helps to make uniform layers (15) When the clays lose moisture, cracks develop and the barrier is ineffective, regardless of the fact that the clay can bind pollutants strongly. This is a serious problem and a quote from a technical report by the U.S. Department of Commerce helps to accentuate the problem: "clay liners may be subject to developing desiccation cracks during and immediately after installation. The clay may be protected from desiccation after construction by installing a synthetic membrane; by installing 1 to 2 feet of soil; or for surface impoundments, by putting liquids into the impound immediately after construction" (16).

SOLUTIONS TO CLAY DILEMMA

Clays are complex reagents and the possibilities to alter physical and chemical properties are endless. This is the direction that the research follows, to reduce the characteristics that contribute to the drawbacks of using clays for various environmental applications. Binding energies need to be measured. Which clay to use or what clay modification scheme is best depends on the energies of adsorption, ΔG_{ads}, ΔH_{ads}, ΔS_{ads}, which are measured for that particular pollutant. Interactions of gases on solid phase clay adsorbents are possible with inverse gas chromatography, IGC, methods that have been applied to clays (8,9). IGC makes physicochemical measurements that provide energies of adsorption and the combination of enthalpy and entropy values help to elucidate reaction mechanisms to make the best choice of the appropriate clay or to better design modified clays for the specific need. If the binding energies of pollutants are measured and they prove to be strong, only then can judgments be made as to whether pollutant encapsulation or adsorption are possible. As another example, the regeneration of the adsorbent may be a critical factor. The ability to regenerate the absorbent material depends heavily on the binding energies. A stronger effort must be made to report these measurements.

In the case of cesium desorption, the reports are primarily from specific geographical regions (10-14). A comprehensive study to involve the whole clay spectrum is needed; the solution is still not at hand. An understanding of the mechanisms of adsorption would include all of the other members of the alkaline earth and alkali metal elements to observe trends. Clay chemistry, i.e. charge, particle size, moisture level, pH, and ion competition must be systematically studied in order to better understand the mechanism of adsorption and conversely the desorption processes that bind cesium so tightly.

To address the second major drawback, the underlying reasons for the swelling need to be revealed. Clays swell because there is a driving force to hydrate the counter-ions.

When the coulombic attractions between clay platelets are overcome by the pressure exerted by the intercalated water, the clay swells and this action renders the clays useless because the packing no longer has hydraulic conductivity. The landfill problems from cracking of the clay liners are due to desiccation and the fundamental hydration process is again the reason for the problem. Exchange of the clay counter-ion by other ions with different hydration energies affects the swelling which in turn alters the adsorption. This action could even be accomplished in-situ. A second method that has been developed in the lab takes advantage of the diverse chemistry that is possible with clays. The swelling and suspending action is eliminated. These new materials have good hydraulic properties that were non-existent before the modification. The adsorption characteristics of these new materials have not been tested yet. A third alternative encapsulates the modified clay in a sol gel. The dried sol gel beads are excellent packing materials; columns packed with these beads have excellent hydraulic properties that are not possible with unmodified clay. Because the sol gel is porous, solvents and pollutants can penetrate the beads to interact with the clays. The selectivity of the clays is still as effective. Benzene, toluene, ethyl benzene, and the xylene isomers were tested. Different encapsulated clays had distinct adsorption capacities for these aromatic compounds (17).

CONCLUSIONS

Clays are effective sorbents for many environmental purposes. Certain drawbacks make them ineffective in special situations. One disadvantage is that the binding to pollutants is not selective or the reverse processes are not understood and cannot be controlled. The other case is that the hydration-dehydration process makes it impossible to take advantage of the adsorption properties of the clays. However, chemical modifications can change the physical and chemical properties to produce new materials that can overcome the drawbacks that were described. These new materials and the ability to measure the binding energies help to eliminate the dilemma of choosing the appropriate clay adsorbents for environmental applications.

REFERENCES CITED

1. Corral, Y.A. and Lara, A.S., "A Comparison of Gibbs Free Energy of Adsorption for Aromatic Compounds onto Three Adsorbents: Graphite, Zeolites, and Layered Clays," in preparation.

2. Brindley, G.W. and Lemaitre, J. and Newman, A.C.D. (editor), *Chemistry of Clays and Clay Minerals, Mineralogical Society Monograph No. 6*, 319-331. New York: John Wiley & Sons, 1987.

3. Mc Bride, M.B. and Dixon, J.B. (co-editor) and Weed, S.B. (co-editor), *Minerals in Soil Environments, Second Edition*, 35-84. Madison: Soil Science Society of America, 1989.

4. Barrer, R.M.,"Shape-Selective Sorbents Based on Clay Minerals: A Review," *Clays and Clay Minerals* **37**, 385-91 (1989).

5. Lara, A.S. and Eiceman, G.A., "Gas Chromatographic Retention Properties of Organoammonium Exchanged Montmorillonites. II. $CH_3N^+H_3$, $(CH_3)_4N^+$, $(CH_3)_3N^+CH_2C_6H_5$ and 1,4-diazabicyclo[2.2.2]octane-$2H^+$," *Journal of Chromatography* **549**, 283-295 (1991).

6. Eiceman, G.A. and Lara, A.S., "Gas Chromatographic Retention Properties of Organoammonium Exchanged Montmorillonites. I. Tetra-alkylammonium Cations," *Journal of Chromatography* **549**, 273-281 (1991).

7. Santana, G. and Lara, A.S., "Energies of Adsorption onto TMA-montmorillonite for the Pentane Isomers," in preparation for *Clays and Clay Minerals* .

8. Lara, A.S. and , "Using Inverse Gas Chromatography to Obtain Thermodynamic Values for Adsorption onto Organoclays," submitted for publication.

9. Pinnavaia, T.J. and Lara, A.S., " Heats and Entropies of Adsorption for Hydrocarbons onto Organoclays," submitted for publication.

10. Sawhney, B.L., "Selective Sorption and Fixation of Cations by Clay Minerals: A Review," *Clays and Clay Minerals* **20**, 93-100 (1972).

11. Zorpette, G., "Hanford's Nuclear Wasteland," *Scientific American*, 88-97 (1996) May.

12. Sawhney, B.L., "Potassium and Cesium Ion Selectivity in Relation to Clay Mineral Structure," *Clays and Clay Minerals* **18**, 47-52 (1970).

13. Oscarson, et. al., "Sorption of Cesium on Compacted Bentonite," *Clays and Clay Minerals* **42** No.6, 731-736 (1994).

14. Staunton, S., "Adsorption of Radiocaesium on Various Soils: Interpretation and Consequences of the Effects on Soil: Soil Solution Ratio and Solution Composition on the Distribution Coefficient," *European Journal of Soil Sciences* **45**,409-418 (1995).

15. Goldman, L.J. and Greenfield, L.I. and Damle, A.S. and Kingsbury, G.L. and Northeim, C.M. and Truesdale, R.S., *Design, Construction, and Evaluation of Clay Liners for Waste Management Facilities*, 5-55. Springfield: U.S. Department of Commerce National Technical Information Service, 1988.

16. Goldman, L.J. and Greenfield, L.I. and Damle, A.S. and Kingsbury, G.L. and Northeim, C.M. and Truesdale, R.S., *Design, Construction, and Evaluation of Clay Liners for Waste Management Facilities*, 5-35. Springfield: U.S. Department of Commerce National Technical Information Service, 1988.

17. Nieves, R. and Lara, A.S., "Encapsulation of a Modified Clay in Silica-Gel Beads," in preparation for publication in *Clays and Clay Minerals*.

Table 1
Gibbs Free Energy of adsorption on graphite and clay, -kJ/mole

Adsorbate	*Graphite*	*Sodium Clay*
benzene	35	31
n-hexane	30	19
pentane		66 on a modified porous clay

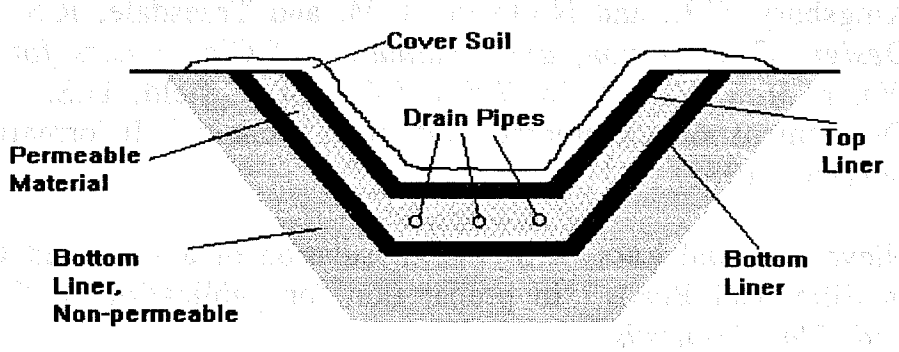

Figure 1. Cross-sectional view of a waste managment facility.

Microbial Enhanced Waterflooding of Low Gravity, Asphaltic Crude Oil: A Southern Oklahoma Case Study

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ABSTRACT

A study of data collected from more than 2,000 commercial microbial enhanced oil recovery (MEOR) projects was conducted in order to determine what effect, if any, oil gravity has on the ability of hydrocarbon-utilizing surfactant-producing bacteria to enhance recovery. The statistical analysis of the data indicated that the process becomes increasingly effective in lower gravity crude oil versus oils with higher gravity (1), and should deliver the best results in crude oil with a gravity at or below 20° API (see Figure 1.). Therefore, a commercial MEOR pilot project was initiated in a mature waterflooded reservoir containing an asphaltic, 18-22° API gravity oil located in southern Oklahoma.

This paper will discuss the results of the MEOR project to date. It will detail reservoir characteristics and discuss the effects of MEOR on oil and water production rates. In addition, the paper will discuss the effects of MEOR on water injection rate and pressure. Economic data including cost per incremental barrel of oil produced, cost per barrel of water injected, return on investment, and payout period will be presented to illustrate that MEOR is an environmentally safe, effective, affordable method of tertiary enhanced oil recovery in low oil gravity reservoirs.

INTRODUCTION

Waterflooding of reservoirs containing low gravity oil are inefficient due to poor oil/water mobility ratio, high surface tension, and high oil viscosity to name a few. It has been demonstrated that chemicals, like surfactant, can be added to the injected water in order to lower surface tension of residual crude to the point that it becomes mobile.

The MEOR process described here has been used in numerous projects to improve waterflood efficiency and its oil release mechanism is very similar to that of conventional chemical surfactant. The primary components of the system include a special mixed culture of dry powder hydrocarbon-utilizing microorganisms and dry granular inorganic growth stimulants that can be added to the existing water injection stream and pumped into the target reservoir. After the MEOR materials have been placed in the reservoir, the microbes seek out crude oil and use it as a source of energy to reproduce and make surfactant byproducts. These surfactants, which are manufactured continuously by the microorganisms within the reservoir pore spaces, improve the mobility of oil by decreasing its interfacial tension to rock/water surfaces. Oil production is enhanced as an incremental amount of previously immobile oil is mobilized and swept to producing wells. As the microbes work their way to producing wells, they may improve the relative permeability of the near-wellbore to oil by softening and removing heavier hydrocarbons that are currently restricting fluid flow.

The MEOR system also improves injectivity in water injection wells because the microbes and their surfactants break down and remove oil and iron sulfide deposits that accumulate in the near-wellbore area over time to restrict fluid entry.

BACKGROUND

The pilot project area is located in the Sho-Vel-Tum Field of Carter and Garvin Counties, Oklahoma near the town of Ratliff City. Fifteen water injection wells have been flooding ninety producing wells since the early 1970's. Well spacing is ten acres. A daily total of 14,000 barrels of water are injected into six different zones of the Tussy Deese Sandstone Formation to produce 650 barrels of oil and 13,000 barrels of water. Several normal faults separate the field into distinct blocks that are not reservoir communicated with one another. Since each block contains at least one water injection well and several offset producing wells, there were multiple locations to choose from for the MEOR pilot project.

The area chosen for the pilot is located on the northernmost end of the waterflooded area and is separated from the rest of the unit by a fault. It consists of one water injection well that floods four producing wells on a 5-spot pattern. Immediately prior to beginning the project, a daily total of approximately 530 barrels of water were injected at a pressure of 300 psi to produce 28 barrels of oil and 500 barrels of water. In this area, the Tussy Deese produces from two, fifteen foot thick zones that are encountered at a depth of -2,100 feet from surface (-1,000 feet subsea). The two zones, which are separated from one another by eight feet of impermeable shale, have average porosity of 25%, 15-20 millidarcies permeability, and a temperature of 100° F.

PRE-MEOR TREATMENT STUDY

The pilot area was tested for MEOR compatibility and quality of reservoir and production/injection data. Prior to beginning the project, representative samples of produced and injected fluids were collected and tested for compatibility with the MEOR materials. Pertinent field and reservoir data was collected and studied, so that treatment strategies could be designed.

"Best-fit" decline trend curves were computer-generated through tabular, historical pre-MEOR production data and extrapolated to establish the base-line for expected future production without the affects of MEOR.

MEOR TREATMENT PROCEDURE

A treatment strategy was designed to utilize the water injection well as the method of delivering the MEOR system to the reservoir. Once every month, a 35 barrel MEOR solution is blended in a bobtail pump truck. Normal water injection is then suspended at the well so that the pump truck can rig up to the tubing and pump the MEOR solution at a rate of approximately two barrels per minute. After the entire MEOR solution has been pumped, the truck rigs down from the tubing and the well is immediately returned to normal continuous water injection operations so that the solution is displaced into the reservoir. A schematic diagram of this treatment technique is presented in Figure 2.

POST-MEOR TREATMENT MONITORING

Oil and water production have been monitored at each of the four producing wells during MEOR in the same manner that they were monitored prior to MEOR. Operator field personnel test each producing well twice a month by collecting a fluid sample in a graduated cylinder. The oil and water are allowed 24 hours to separate from one another. At the end of 24 hours, units of oil and water are counted. Oil units are divided by total fluid units in the graduated cylinder to determine percent oil, and the same is done with water units. Since flow meters are attached to each wellhead to count the total barrels of fluid produced from the well during a 24 hour time period, barrels of oil can be calculated by multiplying percent oil by the total barrels of fluid produced from the well. Daily oil and water production rates were determined for each month by averaging well test data. Production rates from all four producing wells were then summed each month to generate a total average daily production rate for the pilot. Actual oil produced from the pilot since starting MEOR has been monitored and compared to the production volumes defined by the extrapolation of the pre-MEOR historical decline trend curve for the same time period. A total of 24 months of pre-MEOR oil and water production data were used to determine the historical decline trend

of 21% per year. Water production, total fluid production, and percent oil cut have also been monitored at the producing wells.

Water injection rate and pressure have been monitored at the water injection well during MEOR in the same manner that they were monitored prior to MEOR. A flow meter is attached to the injection wellhead to count the total barrels of water injected into the well during a 24 hour time period and a pressure gauge is attached to read injection pressure. Total barrels of water injected per month and average injection pressure are calculated from readings that are recorded daily by Operator field personnel.

RESULTS

Positive production response (incremental production) resulting from MEOR has been defined as actual MEOR oil production in excess of the oil production volumes defined by the extrapolation of the historical decline trend curve. Incremental production does not include any production that has been proven to be the result of a workover, recompletion, increase in water injection rate or pressure, in-field drilling, or any other outside variable that may have influenced production.

The first MEOR treatment was performed in May 1995 and has been repeated once a month thereafter. After MEOR began, oil production gradually increased during the first seven months from a starting rate of 28 barrels per day to a peak daily rate of 40 barrels per day. This represents a 43% increase in oil production. Since peaking, oil production has declined at a rate of 12% per year as opposed to the pre-MEOR decline rate of 21% per year, and during the first 14 months of the pilot project an additional 4,455 barrels (41%) of oil has been produced as a result of MEOR. It has been confirmed that no other outside variable has influenced the project. A graph of monthly oil production is presented in Figure 3.

Prior to beginning MEOR, water production was increasing at a rate of 5% per year. After MEOR began, water production was flat through the first 11 months of the project, and has since begun to decrease. When compared to the daily water production rates that were projected by the extrapolation of the historical inclining trend established prior to MEOR, water production has been decreased by 5%, and the most current water production rate is 19% (nearly 100 barrels per day) below the projected rate of 525 barrels (see Figure 4.). Since water makes up nearly 95% of total production, a graph presenting total barrels of fluid produced per day is not presented as its signature mirrors the water production graph. A graph of average daily oil and water production, and average daily water injection is presented in Figure 5.

Percent oil cut was steadily declining for the two years prior to the start of the MEOR project; however, as is expected with increased oil production and decreased water production, percent oil cut has been increasing for the duration of the project. This is an indication that the relative permeability to oil has been increased by MEOR (see Figure 6.).

Since the MEOR project began, water injection has been maintained at the same rate established prior to the start of the project. Water injection pressure appears to have decreased by an average of 30 psi from the starting pressure of 300 psi, and for the past four months has averaged 60 psi below the starting pressure (see Figure 7.). This represents a 10% and 20% drop, respectively, in water injection pressure. A Hall Plot of cumulative injection pressure versus cumulative barrels of water injected illustrates that a deviation from the pre-MEOR trend has occurred indicating an improvement in injectivity (see Figure 8.). Improved injectivity translates into lower energy cost and less wear-and-tear on equipment.

No negative effects of MEOR have been observed and it has been safe for the oilfield, humans, and the environment.

ECONOMICS

An economic analysis of the data compares the cumulative net value of the incremental oil to the total cumulative cost of the MEOR project. To date, the total cumulative net value of the incremental oil is $44,550 and the total cumulative MEOR cost is $9,450. Currently, the Operators return on investment is 4.7:1 and the MEOR cost to date is $2.12 per incremental barrel of oil produced or $0.013 per barrel of water injected. If the current decline rate of 12% per year is maintained, it is projected that the maximum return on investment will be 11:1, that remaining recoverable reserves will be increased by 200%, and that present discounted value is increased 500%. Project payout was achieved in three months.

CONCLUSIONS

1. This MEOR process is easily applied to pilot areas in existing waterfloods, usually requiring little or no modification of production/injection equipment to accommodate it.

2. The status of MEOR can be easily monitored.

3. This MEOR process has been effective at enhancing the recovery of waterflooded, low gravity oil by 41% (4,455 barrels) to date. It is anticipated that ultimately, MEOR will enhance recoverable reserves by 200%.

4. An increase in oil production and decrease in water production have been observed suggesting improved relative permeability to oil.

5. Water injection efficiency has been improved by lowering the pressure required to maintain water injection rate.

6. This MEOR process is inexpensive. The MEOR cost to date has been $2.12 per incremental barrel of oil produced or $0.013 per barrel of water injected.

7. Operators return on investment to date is 4.7:1 and maximum return on investment is projected to be 11:1. Present discounted worth has been increased 500%.

8. Payout was achieved in three months.

9. No negative affects of the MEOR process have been observed.

10. This MEOR process is safe for the oilfield and the environment. It poses no threat to plants, animals, or humans.

ACKNOWLEDGMENTS

The author wishes to thank Biodynamics Corporation for their permission to publish this paper and salutes innovative oil companies like the Operator of this pilot project.

REFERENCES

Portwood, J. T., "A Commercial Microbial Enhanced Oil Recovery Technology: Evaluation of 322 Project," presented at the Society of Petroleum Engineers Production Operations Symposium, Oklahoma City, Oklahoma, U.S.A., April 2-4, 1995.

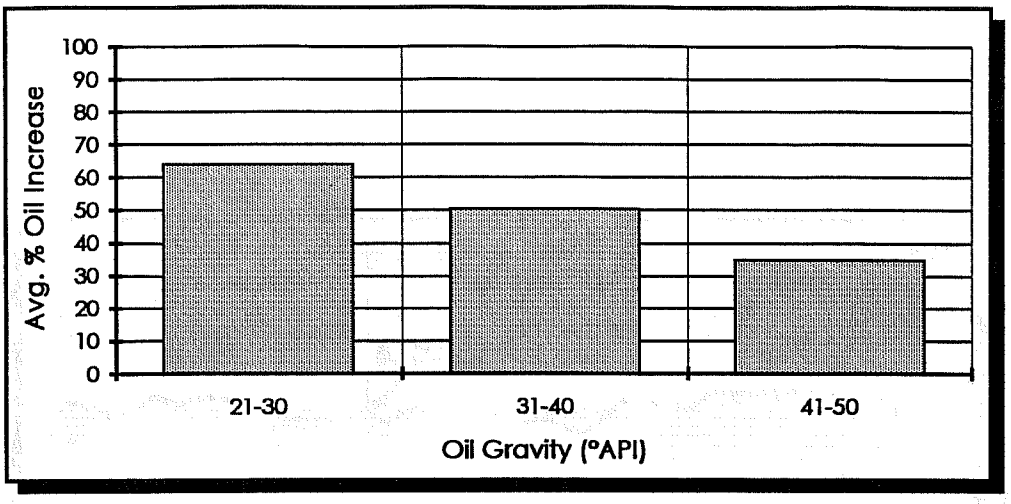

Figure 1. Statistical analysis of MEOR results vs. ranges of oil gravity.

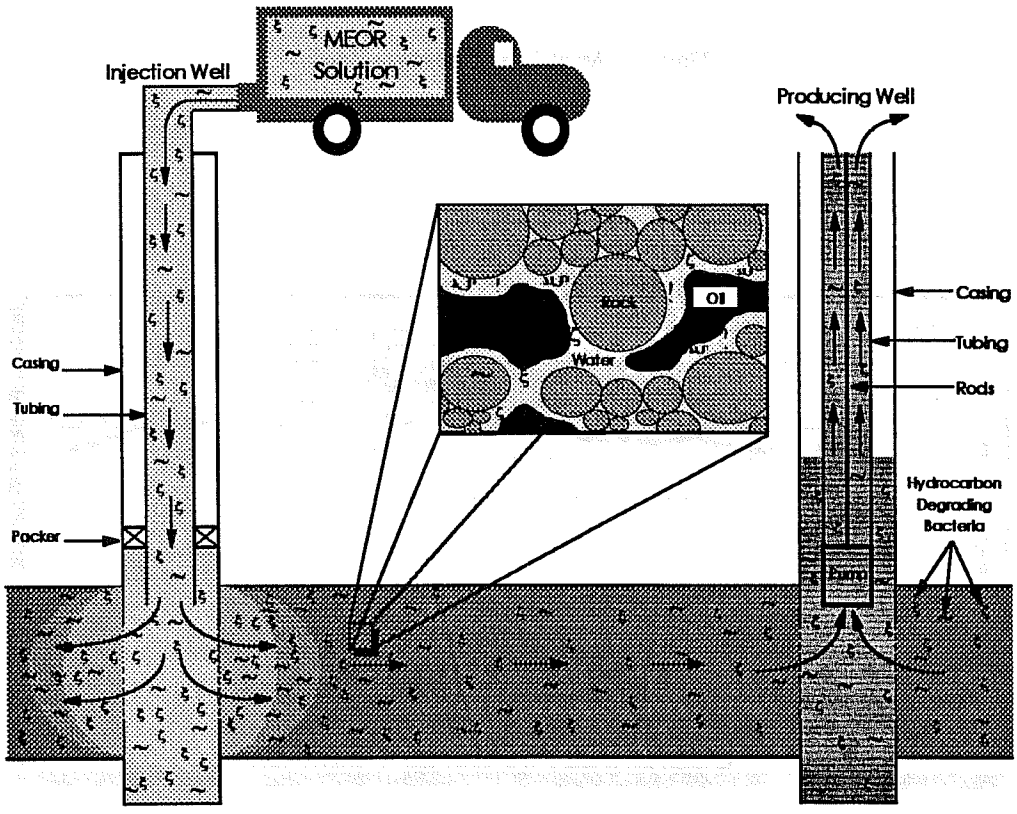

Figure 2. Schematic diagram of MEOR treatment procedure.

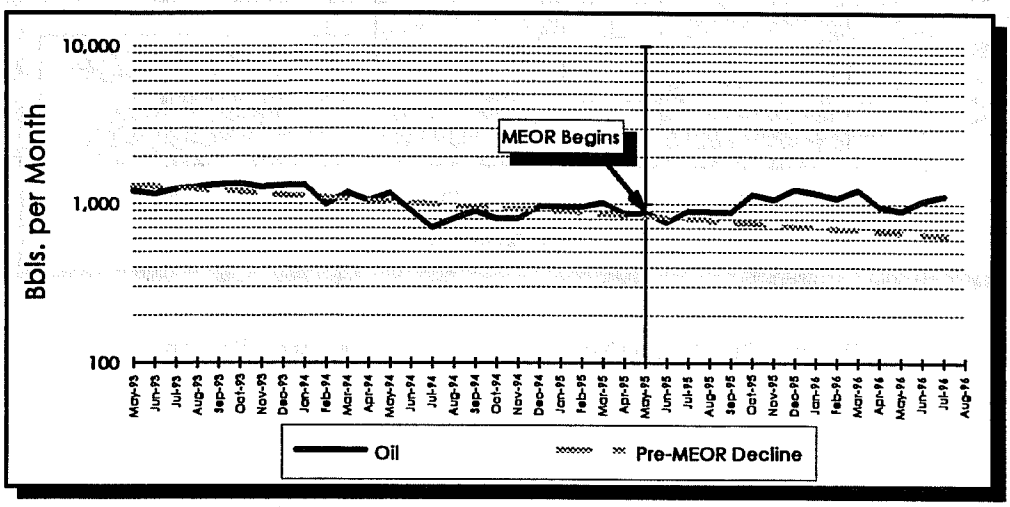

Figure 3. Monthly oil production graph.

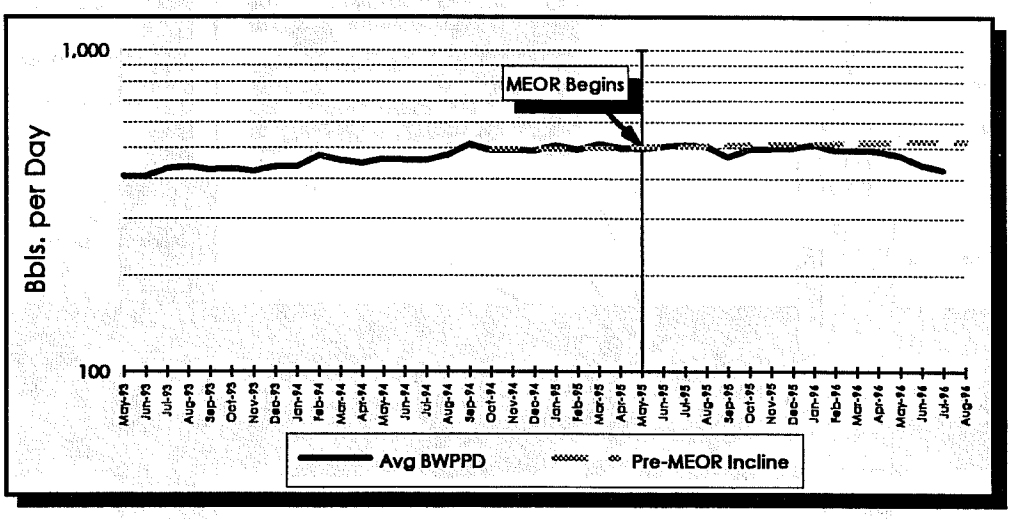

Figure 4. Average daily water production graph.

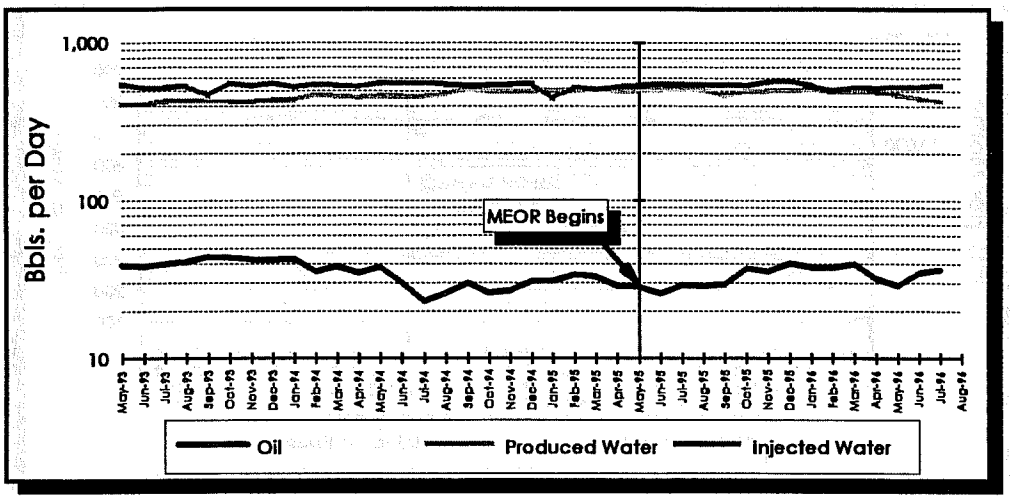

Figure 5. Average daily oil and water production; and average daily water injection graph.

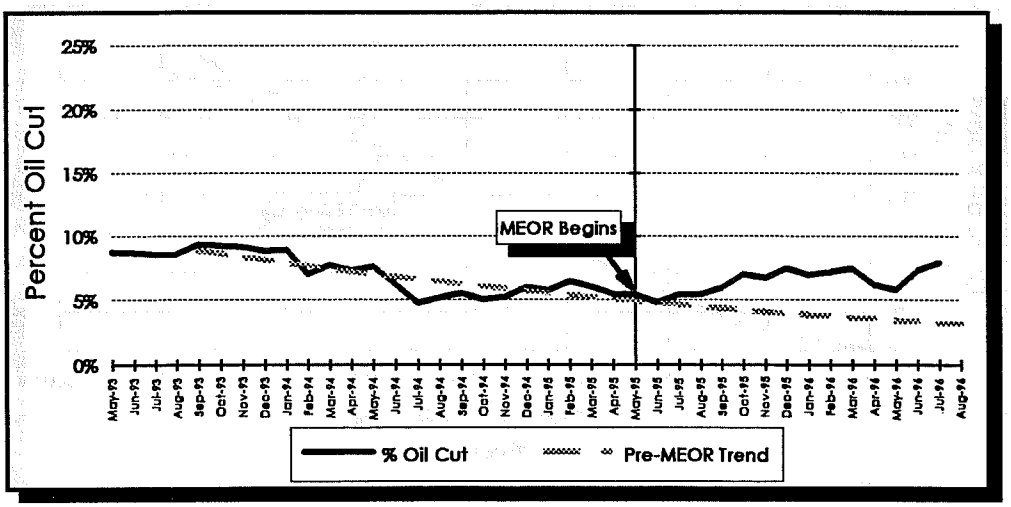

Figure 6. Percent oil cut graph.

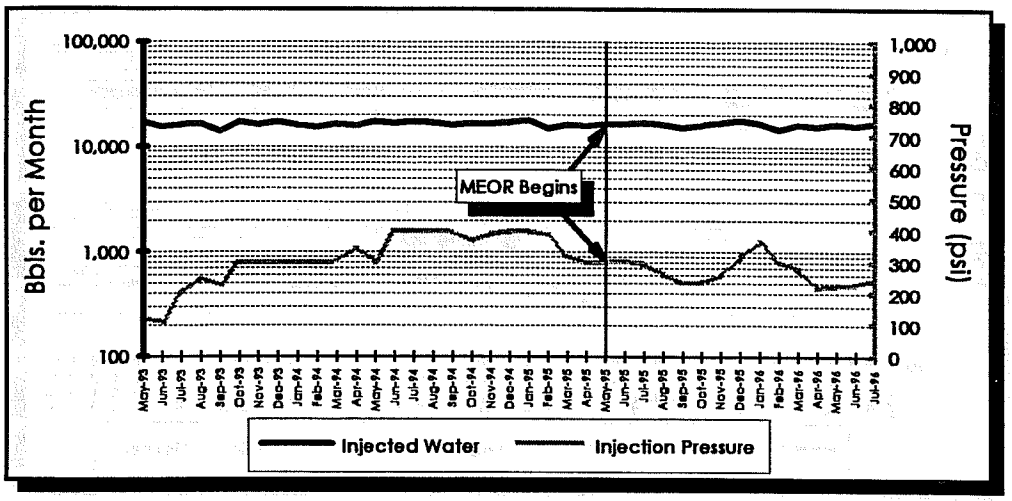

Figure 7. Water injection rate versus pressure graph.

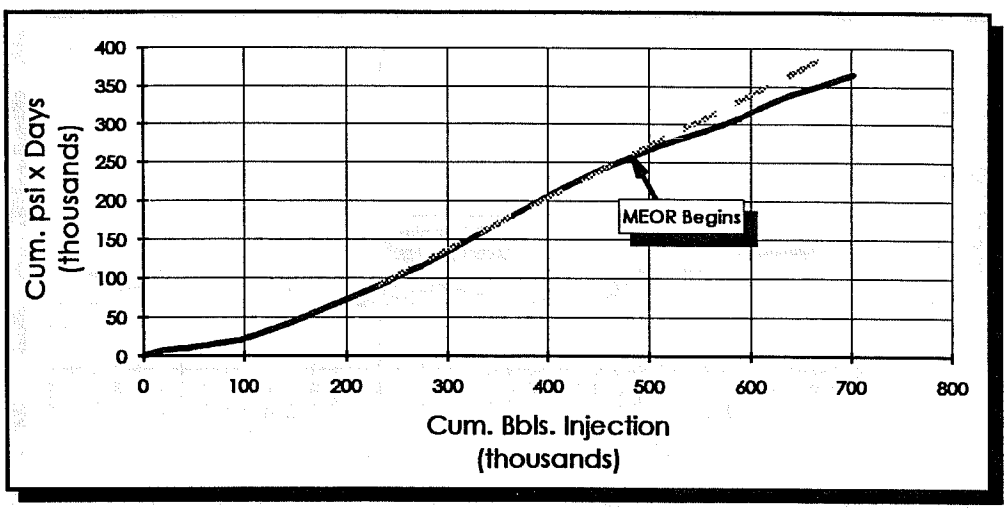

Figure 8. Hall Plot of cumulative water injection volume versus cumulative pressure.

Development of Polymer Gel Barrier for Oil and Ground Spill Containment

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Abstract

Chemical dump sites as well as oil spills occurring in off-shore drilling may contaminate the shoreline several feet below the surface after preliminary clean-up has been accomplished. In New Mexico do not have seas or large rivers on which oil spills might occur, this work will concentrate exclusively on contamination of ground oil spills or chemical leakage from old or illegal dump sites. Further, in New Mexico there are many thousands of abandoned mines, mine dumps and mill tailings ponds. Every one of these has the potential to become a hazard to human activities and to the environment. This class of problem is typical of those existing regionally, nationally, and even internationally.

Testing and development of technology to contain ground chemical and/oil spills continues as a result of local and national concerns. These concerns arise from increased environmental awareness, from accidents during transport, leaking from storage tanks, accidental discharges, etc. The contaminates then migrate to aquifers, thereby risking contamination of both city drinking water, as well as rural aquifers. Contaminants in subsurface water also pose threats to agricultural activities, rapidly migrating higher up the food chain from plants.

The primary objective of the research conducted at UNM is to develop a viscous polymeric gel to act as a sponge to absorb chemical leakage, i.e., effluent from industries and dump sites that contain oil which has seeped into the ground from a spill of a leaking tank or from oil transportation. The gel can then be kept in the ground to contain the oil/chemicals, or microorganisms can be injected into the polymer gel to digest both the oil/chemical and polymer gel. Ideal barriers should be resistant to water and contaminants, with permeability in the order of 10^{-7} cm/s. The permeability reducing characteristics of several promising soil/polymer barriers were studied. Results of this study have shown that the use of organic chemicals as crosslinking agents is much better than that of multivalent metal cations for PAA system. The resultant improved sealing capacities offer a low-cost, reliable, long-term or temporary solution for impervious hydraulic barriers

INTRODUCTION

Most of the world freshwater is at underground. Also, groundwater is a fragile resource and is difficult to remediate, once contaminated. However, groundwater is being seriously contaminated in the United States since 4 to 12% of the 5 to 8 million underground storage tanks in North America that store petroleum products are estimated to be the contamination sources for subsurface soils and groundwater systems [1]. Oils and fuels generally enter the environment as a result of leaking storage tanks and associated piping (both above and below ground) or accidental spills. Prompt removal of accident spills is seldom done, and leaking storage tanks and piping is hardly detected promptly. And hence the spilled and leaked hydrocarbons will leach into underground, and pollute our water supply. Petroleum hydrocarbons (PHC) have limited solubility, micelles can be formed in water and produce hydrocarbon-like domains. Much more hydrocarbons can be contained in water than predicted by the PHC solubilities [2-4].

There are various techniques for contamination treatment. Each has its own limitations and development of new technologies is needed. At the present time, the available techniques involve controlling the flow of the polluted groundwater; physical containment of the material; removing contaminated soil to a secure site; in situ treatment by physical, chemical, or biological technologies; withdrawal of groundwater followed by surface treatment; or a combination of these. Costly removal may be applicable only to relatively small contaminated area. Further, removal is not a permanent solution to contamination and merely moves the problem from one place to another. To solve the contamination problem completely, remediation techniques, such as chemical method, have to be used to treat the soils. Protection of aquifers from oil contamination is probably the best solution to the problem, since cleanup of contaminated groundwater is likely to be difficult and expensive. However, once groundwater pollution has occurred, there are a number of technologies that can be used to cleanup the contamination [5-7]. Besides the use of retention barriers, a wide range of engineering technologies and options are available for the treatment of petroleum hydrocarbon contamination. These options include: soil washing [8, 9], soil venting [10], vapor extraction [11], thermal treatment [12-14], and bioremediation [15-18]. Generally, before site remediation is processed, a retention barrier wall will also be constructed to prevent continuing groundwater contamination and hence lower the remediation costs [19].

Retention is a temporary method for controlling the migration of contaminants. And containment barrier technology is used. Contaminant transport through a barrier includes advection, dispersion, sorption and decay. Barriers can be divided into two categories, passive barriers and active barriers. Passive barriers prevent the contaminants from leaching into groundwater or contaminant migration with groundwater flow, by reducing the permeability of the site. They may consist of one or more components such as geomembranes, diaphragms, sheetpiles, slurry trench cutoff walls, grout curtains [20, 21], or even tensiometric barriers (dry barriers) [22]. Active barriers, such as chemical barriers [23-25] and biological barriers [26], reduce the effect of contaminants on the surrounding environment by reacting with the wastes when they migrate through the barriers. One of the advantages of using active barriers is that the barriers do not substantially change the flow pattern of groundwater.

Cement-based barriers are the most common of the passive barriers [27]. Its disadvantage is the high costs of pumping to inject cements into the ground; and, its advantages include that the materials set hard and be water resistant. Cement

consolidation requires 25-60% water and thus eliminates dewatering of the site for consolidation. Adsorbing materials such as bentonite can be added, provide enhanced surface area and cation exchange capability. Many organic and inorganic compounds are bound by sorption. Metals are immobilized by formation of hydroxides or basic carbonates. However, cement mixtures have a high pH>12 and certain toxic metals (Pb, Cr, Cu, Ni in particular) show increased solubility at pH>12. Hence, transport of these metals can be enhanced by a cement barrier as can dissolution products of humic acid complexes. The setting of cements can be retarded by organic solvents, oils, sulfates, and halides.

Conventional barrier construction by grouting or slurry wall techniques requires either excavation or pumping or both of highly viscous substances (e.g. cement) and hence are radically limited by excessive costs and the shallow depths that can be reached. The low viscosity and controllable gelation of the barrier material proposed in the next section will allow the use of larger numbers of deeper drill holes other than has been used to date. The polymer will penetrate much further into soils and fractured rock while ungelled. Hence the engineering of particular barriers with specific shapes and other characteristics will be far easier than with conventional costly and limited techniques. The actual geometry of the barrier (the bore hole drilling and injection procedures) will be determined by using site hydrological and contaminant plume and migration studies as well as by the particular barrier construction technique employed [28].

Water glass polymers can significantly inhibit the migration of transitional metal contaminants; but are ineffective for chloride and monovalent cations. Heat for injection is involved in constructing thermoplastic barriers. Its limitations include high cost for pump power and heating. Further, undesirable reactions during heating process can produce new pollution components. The oil industry has used organic polymers for tertiary recovery due to their high viscosity, density and immiscibility with water [29]. The main problem using these organic polymers is that some organic solvents and oils may retard (but not prevent) gelation. For the proposed application, the viscosity has to be low before gelation to significantly reduce power requirements for injection as to be able to construct larger barriers.

Impervious barriers between the oil contaminants and adjacent soil and groundwater can be constructed using polymer gels. The barrier is formed by injection into the ground an ungelled (hence low viscosity) polymer-crosslinking agent mixture, which will then gel in controlled fashion to reduce the operation cost. In this study polymer gels have been developed as hydraulic barriers to stop or at least significantly retard the migration of contaminants in the soil. The barrier will be constructed by injection into the ground of ungelled polymer solution (for reduction of pumping cost), which will then gel in controlled fashion in situ. The effective porosity of the polymer gel barriers can either be tested or assumed to be almost the same as that of soil in situ because the main component of the polymer gel is water. Cu^{2+}, Cd^{2+} and Zn^{2+} have been selected as model contaminants.

MATERIALS AND METHODS

Polymers and other gel forming materials include Polyox (Union Carbide Co.), Sodium silicate (J.T. Baker Inc.), Polyacrylamide (American Cyanamid Co.), Jaguar 8836 (Rhone-Poulec Inc.), Rhodopol 23 (Rhone-Poulec Inc.), etc. Several cross-linking agents were used to provide controllable cross-linking process. They include Borax, Tyzor (Du Pont Chemicals), Glyoxal, Chromium Chloride, Ferrous and Ferric Chloride, Glutaric dialdehyde, Formaldehyde, etc. The chemicals used for pH control or gelation control included Tri-sodium phosphate, Ammonium hydroxide, Sodium hydroxide, Acetic, Sulfuric, and Hydrochloric acid.

Density was measured by the standard pycnometer method, using tap water as a reference at ambient temperature, (density 0.997 g/ml). Viscosity was measured by two methods at ambient temperature, the Thomas-Stormer viscometer and the Boekel (Zahn cup-type) viscometer.

The permeabilities of three PAA gels crosslinked by Cr^{3+}, glyoxal, or glutaric dialdehyde were measured. The gel was made by mixing crosslinking agent with PAA solution. The pH of PAA solution was adjusted by adding NaOH (2.5 M) or HCl (2M) for the control of the gelation time. The formulation of these three PAA gels and the pH of PAA solution before the addition of crosslinking agent are as follows. (1). PAA-Cr^{3+} (PAA-Cr) gel: PAA 4.5% (w/v), Cr^{3+} 110 mg/L, pH=5.6; (2). PAA-Glyoxal (PAA-G) gel: PAA 4.5% (w/v), Glyoxal (40% v/v) 3.5% (v/v), pH=9.4; (3). PAA-Glutaric Dialdehyde (PAA-GD) gel: PAA 4.5% (w/v), Glutaric Dialdehyde (25% v/v) 1.6% (v/v), pH=10.8. The permeability was tested using the falling head method. The permeability of the sand pack used to support the gel was measured using the constant head method. For the simulation of the effect of soil on the permeability of the polymer gels, the permeability of sand-polymer gel mixtures were also tested. The polymer gel/sand barriers were made by mixing ungelled polymer-crosslinking agent solution with sand directly. The volume ratio of sand to polymer gel was 1:1.

The diffusion coefficients of metal ions (all are sulfates), Cd^{2+}, Cu^{2+} and Zn^{2+}, in the polymer gel were determined using lag time analysis [30]. For the estimation of effective diffusion coefficients of metal ions in the soil gel barrier, the diffusion coefficients of metal ions in the PAA-Cr gel with different amounts of wax were measured. The procedure to make the gel barriers is as follows: PAA polymer powder was dissolved completely in water, and its pH was adjusted to 5.6 by adding HCl (2M) in order to control the gelation time. The solution was then mixed with high concentrated $CrCl_3$ solution (1000 mg/L of Cr). The composition of the PAA-Cr gel is: PAA 4.4% (w/v), Cr^{3+} 110 mg/L. Different amounts of wax were mixed with ungelled PAA-Cr solution to make 4 types of gel/wax barriers. The wax was reduced to particles with diameter about 0.5 mm before being mixed with PAA-Cr solution. The volume percent of the wax in the gel/wax barrier (GW) are: 7.3%, 12.8%, 17.7%, and 22.7% for barrier GW1, GW2, GW3, and GW4 respectively.

A few promising candidate gels have been selected out of several hundreds. As indicated in Table 1, the viscosity increases dramatically after gelation, sometimes exceeding the limits of the viscometers used, or even becoming solid [31]. Since the main component of the gel is water, the density of the gels at ambient temperature is similar to or slightly higher than that of tap water.

RESULTS AND DISCUSSION

Polyacrylamide (PAA) can be easily crosslinked to form a polymer gel barrier. Thus it is a promising polymer material. Cr^{+3} and Al^{+3} are the common crosslinking agents for PAA gel. However, we found that either Fe^{+2} or Fe^{+3} is also an effective crosslinking agent and has the advantage of being less toxic and cheaper. Extensive experiments have been performed in our laboratory to study PAA gels which will be described below.

Cr^{+3} and Al^{+3} are the usual crosslinking agents for this gel. In searching for less toxic and cheaper crosslinking agents, we have tested Fe^{+2} and Fe^{+3} and have found that either Fe^{+2} or Fe^{+3} is also an effective crosslinking agent, and has the advantage of being less toxic and cheaper. As the solubility product (Ksp) of ferric Fe, $Fe(OH)_3$, is very small (about 1.1×10^{-36}). At a pH of 2 to 3, most of the Fe^{+3} is hydrolyzed and is not free. At higher ph $Fe(OH)_3$ precipitates. The ferrous form, $Fe(OH)_2$, is much more soluble (Ksp = 1.6×10^{-14}) and provides even higher solubility than that of Al^{+3} as $Al(OH)_3$ (Ksp = 1.1×10^{-15}) or Cr^{+3} as $Cr(OH)_3$ (Ksp = 3.0×10^{-29}) [32]. Hence the ferrous form of Fe can provide much wider pH range for effective gelation.

A marked inverse dependence of the gelation time on pH was found. If the pH is lower than that at which Fe^{+2} begins to hydrolyze. Visible inspection verified the formation of colloidal deposit in the nongeling solutions with pH larger than 6. Hence we suggest that the colloidal form of Fe^{+2} is inactive in crosslinking. A significant inverse dependence of the gelation time on the concentration of crosslinking agent (from 50-400 ppm) was also found at pH 5.8 with fixed PAA concentration (2%, hydrolyzed). The effect of concentration of PAA on the gelation time was examined at pH 5.8 with a fixed concentration of crosslinking agent Fe^{+2} (200 ppm) at room temperature. No gel will be formed if the concentration of PAA in solution is less than 1%, even after 10 days. And there is almost no effect on the concentration from 2% to 5% on the gelation time. The gelation time is significantly affected by the concentration of crosslinking agent.

Amide groups in the polyacrylamide polymer can react with dialdehydes under basic condition. Hence glyoxal was used to crosslink PAA polymer because it is the lowest cost dialdehyde. The gels formed are clear and have no color if the pH is lower than 11, otherwise, the gels are yellow. The effect of pH on the gelation time was studied as follows: 2 g PAA was dissolved in 40 ml tap water with different pH adjusted with NaOH or $Na_3PO_4 \cdot 12H_2O$. 1.5 ml glyoxal (40%) was then added into this solution based on the acrylamide units in the polymer. The gelation time was determined by visual observation (Fig. 1). Gelation time can be decreased significantly by adding of soil. 40 g soil with different ph were added to 40 ml of PAA polymer solution (5%) and mixed with 1 ml glyoxal (40%). 1.5 M HCl was added to adjust the pH of soil. The soil was then dried in an oven at 120 °C for 2 h. Unfortunately, the soil gel barrier would break and leak water after several days or several weeks. However, inert ground layers or other types of soil may be suitable for this type of gel.

Glutaric dialdehyde was also used to crosslink PAA polymer. The gel formed is brown or yellow. The higher the pH, the shorter the gelation time, and the darker the color. The effect of pH on the gelation time of PAA gel was studied as follows. 2 g PAA were dissolved in 40 ml tap water. NaOH or $Na_3PO_4 \cdot 12H_2O$

or HCl was used to adjust the pH. 2 ml glutaric dialdehyde (25%) was then added into this solution based on the acrylamide units in the polymer. Visual observation was used to determine the gelation time and the results are shown in Fig. 2.a. It was found that it gels only if the pH is higher than 10. Fig. 2.b shows the details in the pH range from 11 to 12. Also, as has been shown in Fig. 2, that the soil will affect the gelation time significantly. The experimental procedure was as follows. 2 g PAA polymer powder was dissolved in 40 ml tap water with different pH adjusted with NaOH or $Na_3PO_4 \bullet 12H_2O$ or HCl. 2 ml glutaric dialdehyde (25%) was then added into this solution based on the acrylamide units in the polymer and mixed. Last, 40 g SNL soil (pH is about 7.6) were added. This type of soil/gel barrier was very strong and stable over the experiment time period (about one year).

Acrylamide monomer can react with aldehydes to give the corresponding alkylidenebisacrylamides under acidic conditions. So, formaldehyde was used to crosslink PAA because formaldehyde is low in cost compared with glyoxal and glutaric dialdehyde. The gel formed is clear. The experimental procedure was as follows: 2 g PAA polymer powder were dissolved in 40 ml tap water with the pH adjusted with HCl. 1 ml formaldehyde (37%) was then added to this solution based on the acrylamide units in the polymer. It has been found that a strong gel will form in 4-7 h in the pH range from 2 to 7. The effect of pH on the gelation time is not very significant compared with other PAA system. A possible reason is the buffering effect of the imidization reaction/hydrolysis of PAA with H^+/OH^-. The gelation time is increased significantly by adding soil (40 g SNL soil), but a good soil/gel will also form in about 6 days in the pH range from 2 to 7.

In summary, if pH is lower than that at which Fe^{+2} begins to hydrolyze, there is a marked inverse dependence of the gelation time on pH. Also, there is a significant inverse dependence of the gelation time on the concentration of crosslinking agent. On the other hand, the PAA concentration has no significant effect on the gelation time if it is above the lowest limit. However, it will affect the strength of the gel formed [31]. Organic solvents can also be used to crosslink PAA polymer. For example, amide groups in the polyacrylamide polymer can react with dialdehydes, such as glutaric dialdehyde and glyoxal under basic condition, and crosslinked PAA polymer gel is then formed. pH of the ungelled polymer-crosslinking agent mixture can changed to adjust the gelation time. The gelation time can be decreased significantly by some types of soil. Aldehydes can react with acrylamide monomer to give the corresponding alkylidenebisacrylamides under acidic conditions. Hence, formaldehyde is also a promising agent which can be used to crosslink PAA. Further, formaldehyde is cheaper than glyoxal and glutaric dialdehyde. However, the effect of pH on the gelation time is not very significant compared to other PAA systems. The possible reason is the buffering effect of the imidization reaction (hydrolysis of PAA with H^+ /OH). Also, the gelation time is increased significantly by addition of soil [33].

The permeabilities of different PAA gels, PAA gel/sand barriers, and the supporting sand pack were measured. The values determined experimentally at ambient room temperature (22°C) were calibrated to the values corresponding to an average temperature of the groundwater of 10°C. The permeability of the supporting sand pack was $1.2*10^{-3}$ cm/s. The data for the PAA gel barriers are listed in Table 2. The results show a 5 to 6 order of magnitude lower permeability than that of sand pack. The permeabilities range from 10^{-8} to 10^{-9} cm/s, and demonstrate that PAA gels are promising hydraulic barriers. The permeabilities of gel/sand barriers are even lower than those of pure gels. This is perhaps because of the strength increase of the gel barriers after polymerizing with hard solid particles.

The effective diffusion coefficients of Cu^{2+}, Zn^{2+}, Cd^{2+} in PAA-Cr gel and gel/wax barriers were measured using the lag time method. The data are shown in Table 3. The control data of diffusion coefficients of metal ions in water are also listed [34]. Generally, the reduction in diffusion coefficients of metal ions in the PAA-Cr gel compared to the corresponding diffusion coefficients in water can be entirely attributed to the reduction of available volume to a fraction, ε, of the total gel volume and an increase in path length for diffusion by a factor of τ (tortuosity factor): $D_{gel} = D_{water}\ \varepsilon/\tau$. Table 3 shows that the diffusion coefficients of metal ions in the 4.5% PAA-Cr gel are about 30% lower than those in water. This is mainly because of the structure characteristics of the crosslinked gel which affect the diffusion by the tortuosity factor (τ is about 1.3 to 1.4) and because the porosity of the polymer gel is near 1 (ε is about 0.955). The effective diffusivity of metal ions in the gel/wax system and the diffusion coefficients in the PAA-Cr gel can also be related by a similar equation: $D_{eff} = D_{gel}\ \varepsilon/\tau$

Oil droplets floating on the groundwater are easily contained by the polymer gel barrier. However, oil derivatives dissolved in groundwater can migrate through the gel barrier by effective molecular diffusion. The monoaromatic hydrocarbons represent a significant potential source of groundwater contamination, especially in gasoline spills. They include benzene, toluene, ethylbenzene, and three xylenes, m-, o- and p- as a group termed BTEX. These constitute the most soluble and most mobile fraction of gasoline; benzene has a very low allowed level in drinking water of 5 μg/L due to its carcinogenicity. The effective diffusion coefficients of soluble components in the oil, such as BTEX, are needed for the estimation of their migration through the gel barrier. However, the data are not available from the literature. One probable reason is that the USEPA-approved analysis procedure for BTEX is not simple and may easily result in error [35]. Molecular weight of those common components found in petroleum products is much lower than 2×10^4. Hence, it is reasonable to conclude that they can diffuse freely through the PAA gels as discussed above. The values are in the order of 10^{-5} cm^2/sec.

CONCLUSIONS

Migration of spilled PHC occurs both horizontally and vertically. When the migrating PHC is trapped in pores, isolated blobs or droplets will be formed. If bulk PHC becomes entrapped below the water table, soluble PHC components will be dissolved by flowing ground water and carried away from the spill zone. This will lead to continuing groundwater contamination. Generally, these components have lower levels of adsorption to soil particles. The polymer gel barrier is a promising technique to prevent aquifers from contamination by oil. Several different types of potential barrier gels have been selected based on the criteria proposed. The density of the gels are slightly higher than that of tap water under ambient condition. Generally, for the system of PAA crosslinked with different crosslinking agents (multivalent metal ions and organics), the gelation time can be adjusted by the pH and the concentration of crosslinking agents. PAA gels have been found to be promising gel barriers because their permeabilities are of the order of 10^{-8} to 10^{-9} cm/sec, and they are easy to construct.

Acknowledgements

This work has been supported by a grant from WERC of New Mexico and DOE.

Table 1

Density and viscosity measurements
at ambient temperature of various gels (water density 0.997 g/ml)

Gel Mixture	Density of Gel (g/ml) (± 0.002 g/ml)	Viscosity of Gel (cp)
J6, B6	1.001	> 230000
J6, B6	0.999	> 5600
J6, T201	0.999	> 150000
R20, CC	0.998	solid
R20, AK	1.001	> 1400
R20, F3	1.000	> 28000
R20, T201	1.003	> 3000
PAA, F2	1.003	> 112000
PAA, AK	1.005	> 140000
PAA, F3	1.009	> 29000
PAA, GST	1.005	> 230000
PAA, CC	1.009	>230000
SS, A1	1.067	solid
SS, A2	1.043	soliD

Table 2

Permeabilities (K_{10}) of PAA gel barriers

	Pure gel (cm/s)	Gel/sand (cm/s)
PAA-Cr	$1.7*10^{-8}$	$4.9*10^{-9}$
PAA-G	$1.1*10^{-8}$	$3.6*10^{-9}$
PAA-GD	$1.0*10^{-8}$	$2.3*10^{-9}$

Table 3

Effective diffusion coefficients of metal ions in the gel barriers
at 22°C (in unit of 10^{-6} cm^2/s)

	Water	Pure gel	GW1	GW2	GW3	GW4
Cu^{2+}	6.60	4.48	3.96	3.83	3.77	3.63
Zn^{2+}	6.72	4.84	3.96	3.75	3.58	3.24
Cd^{2+}	6.63	4.71	4.02	3.80	3.65	3.30

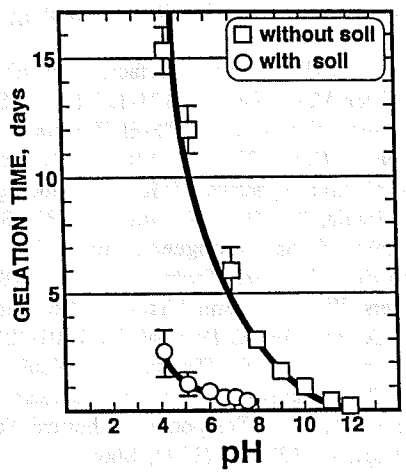

Figure 1

Effect of pH on the gelation time of PAA gel crosslinked by glyoxal

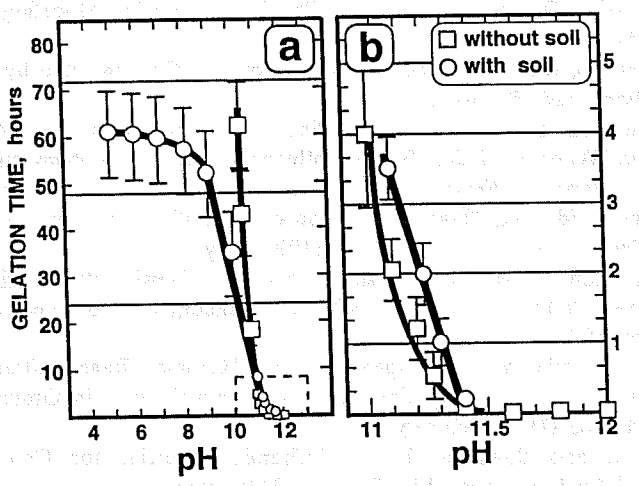

Figure 2

Effect of pH on the gelation time of PAA gel crosslinked by glutaric dialdehyde

References

1. PEI Associates Inc., Handbook of Underground Storage Tank Safety and Correction Technology, Washington. USA, Hemisphere Publishing Corporation, 1988.
2. Yong, R. N. and Rao, S. M., "Mechanistic Evaluation of Migration of Petroleum Hydrocarbon Contamination by Soil Medium," *Can. Geotech. J.*, 28, 84-91 (1991) February.
3. Mackay D. and Shiu, W. Y., Hydrocarbon Contaminated Soils and Groundwater, Vol. 2, 137-154, Chelsea, MI., USA, Lewis Publishers Inc., 1992.
4. Lee, J. F., Mortland, M. M., Chiou, C. T., Kile, D.E and Boyd, S. A., "Adsorption of Benzene, Toluene, and Xylene by Two Tetramethylammonium Smectites Having Different Charge Densities," *Clays Clay Miner.*, 38, 113-120 (1990) April.
5. Ripper, P. and Fruchtenicht, H, "Removal of the Groundwater Pollution Below an Abandoned Waste Oil Refinery," *Water Sci. Technol.*, 21, 1841-1844 (1989).
6. Borden, R. C., Borden, R. C. and Kao, C.-M., "Evaluation of Groundwater Extraction for Remediation of Petroleum-contaminated Aquifers," *Water Environ. Res.* 64, 28-36 (1992) January.

7. Reddy, K., Zhou, J. and Kosgi, S., "New Model to Simulate Air Sparging for Groundwater Remediation," presented at the 5th Annual WERC Technology Development Conference, Las Cruces, NM, USA, April 18-20, 1995.
8. Ang, C. C. and Abdul, A. S., "FOCUS: Aqueous Surfactant Washing of Residual Oil Contamination from Sandy Soil," *Ground Water Monit. Rev.* 11, 121-127 (1991) Spring.
9. Bhandari, A., Dove, D. C. and Novak, J. T., "Soil Washing and Biotreatment of Petroleum-Contaminated Soils," *J. Environ. Eng.*, 120, 1151-1169 (1994) September.
10. Hinchee, R.E., Downey, D.C. and Aggarwal, P.K., "Enhancing Biodegradation of Petroleum Hydrocarbons Through Soil Venting," *J. Hazard. Mater.*, 27, 315-326 (1991) August.
11. Garcia-Herruzo, F., Gomez-Lahoz, C. and Rodriguez-Maroto, J.M., "Influence of Water Evaporation on Soil Vapor Extraction (SVE)," *Water Sci. Technol.*, 30, 115-118 (1994).
12. Bucala, V. Saito, H. and Peters, W. A., "Thermal Treatment of Fuel Oil Contaminated Soils Under Rapid Heating Conditions," *Environ. Sci. & Technol.* 28, 1801-1807 (1994) October.
13. Troxler, W. L., Cudahy, J. J. and Zink, R. P., "Treatment of Nonhazardous Petroleum-Contaminated Soils by Thermal Desorption Technologies," *J. Air Waste Manage. Assoc.*, 43, 1512-1525 (1993)
14. Ayen, R. J. and Swanstrom, C. P., "Low Temperature Thermal Treatment for Petroleum Refinery Waste Sludges," *Environ. Prog.*, 11, 127-133 (1992) May.
15. Shaw, B., Black, C. S. and Mill, C. H., "Microbes Safely, Effectively Bioremediate Oil Field Pits," *Oil Gas J.*, 93, 85-88 (1995) January 30.
16. Li, K. Y., Xu, T. and Verramachaneni, P. B., "Field Test and Mathematical Modeling of Bioremediation of an Oil-contaminated Soil," *Waste Manage.*, 14, 561-570 (1994).
17. Li, K. Y., Xu, T. and Verramachaneni, P. B., "Field Test and Mathematical Modeling of Bioremediation of an Oil-contaminated Soil - Part 2: Mathematical Modeling," *Waste Manage.*, 14, 571-580 (1994).
18. Shen, J. and Bartha, R., "On-site Bioremediation of Soil Contaminated by No. 2 Fuel Oil," *Int. Biodeterior. Biodegrad.*, 33, 61-72 (1994)
19. "Horizontal Wells Can Lower Costs of Remediating Soil, Groundwater," *Oil Gas J.*, 91, 65 (1993)
20. Mott, H. V. and Weber, W. J. Jr., "Factors Influencing Organic Contaminant Diffusivities in Soil-bentonite Cutoff Barriers," *Environ. Sci. Technol.* 25, 1708-1715 (1991) October.
21. Acar, Y. B. and Haider, L., "Transport of Low-concentration Contaminants in Saturated Earthen Barriers," *J. Geotech. Eng.*, 116, 1031-1052 (1990) July.
22. Pringle, S., Thomson, B., Morris, C. E. and Stormont J., "Tensiometric Barriers for Containment at Waste Sites," presented at the 5th Annual WERC Technology Development Conference, Las Cruces, NM, USA, April 18-20, 1995.
23. Morrison, S.J., Tripathi, V.S. and Spangler, R.R., "Coupled Reaction/transport Modeling of a Chemical Barrier for Controlling Uranium (VI) Contamination in Groundwater," *J. Contam. Hydrol.*, 17, 347-363 (1995) February.
24. Morrison, S. J. and Spangler, R. R., "Chemical Barrier for Controlling Groundwater Contamination," *Environ. Prog.*, 12, 175-181 (1993) August.
25. Fryar, A. E. and Schwarte, F. W., "Modeling the Removal of Metals From Groundwater by a Reactive Barrier: Experimental Results," *Water Resour. Res.*, 30, 3455-3469 (1994) December.
26. Kao C-M. and Borden, R. C., "Use of Biological Active Barriers For In Situ Treatment of Contaminated Groundwater," *Water Sci. Technol.*, 26, 2325 (1992).
27. Louvel-Delattre F., Lapeyre C., Struilou R., Retention Mechanisms for Toxications Using Artificial Confinement Barriers of Clay-Cement Mixtures. *Engineering Geology*. 1993; 34:151.
28. Xanthakos, P. In: Slurry Walls. McGraw-Hill Inc. NY 1979.
29. Moradi-Araghi A., Beardmore D. H., Stahl G. A. In: Stahl G. A., Schulz D. N. Ed. Water-Soluble Polymers for Petroleum Recovery. Plenum, New York: 1988:299.
30. Hannoun, B. J. M. and Stephanopoulos, G., "Diffusion Coefficients of Glucose and Ethanol in Cell-free and Cell-occupied Calcium Alginate Membranes," *Biotechnol. Bioeng.*, 28, 829-835 (1986)
31. Wilkins, E. and Lu, Y., "Development of Polymer Gel Barrier for Containment of Hazardous Waste," *J. Environ. Sci. Health Part A*, 29, 1829-1841 (1994).
32. Weaest, R. C. (Ed.). Handbook of Chemistry and Physics. (CRC., Cleveland, 1974), 54th Edition.
33. Wilkins, E., Lu, Y., Dwyer, B. P., Hersman, L. and Wagner, S., "Polymer Gel as a Barrier for Ground Spill Containment," *J. Environ.Con.Des.Man.*, 3, 83-92 (1994).
34. Li, Y-H, and S. Gregory. "*Geochim.Cosmochim. Acta.* **38**(1974), pp. 703-714.
35. Tanaka, H., Matsumura, M and Veliky, I. A., "Diffusion Characteristics of Substrates in Ca-alginate Gel Beads," *Biotechnol. Bioeng.*, 26, 53-58 (1984) January.

Environmental Significance of Biocatalytic Conversion of Low Grade Oils

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ABSTRACT

Studies dealing with the interactions between extremophilic microorganisms and crude oils have led to the identification of biocatalysts which through multiple biochemical reactions catalyze desulfurization, denitrogenation, and demetalation reactions in oils. Concurrently, the oils are also converted to lighter oils. These complex biochemical reactions have served as models in the development of the crude oil bioconversion technology to be applied prior to the treatment of oils by conventional chemical processes. In practical terms, this means that the efficiency of the existing technology is being enhanced. For example, the recently introduced additional regulation for the emission of nitrogen oxides in some states restricts further the kinds of oils that may be used in burners. The biocatalysts being developed in this laboratory selectively interact with nitrogen compounds, i.e. basic and neutral types present in the oil and, hence, affect the "fuel NOx" production. This, in turn, has a cost-efficient influence on the processed oils and their consumption. In this paper, these cost-efficient and beneficial effects will be discussed in terms of produced oils, the lowering of sulfur and nitrogen contents, and the effect on products, as well as the longevity of catalysts due to the removal of heteroatoms and metal containing compounds found in crudes.

INTRODUCTION

In the industrialized and newly industrialized countries, petroleum continues to be a major energy resource. The projected petroleum consumption is steadily on the increase worldwide (1). The environmental impact associated with increasing petroleum utilization is going to increase significantly. Concurrently, federal and state agencies are already imposing tighter regulations on the production and utilization of petroleum to assure a cleaner environment (2).

Chemically, the oil fractions containing organic nitrogen, sulfur, and oxygen compounds (NSO) contribute to environmental pollution because their combustion products, e.g. nitrogen oxides NOx and sulfur oxides SOx, are the major air contaminants. Fractions of crude oil rich in NSO compounds are associated with heavy crude oils (3). Refining of such heavy crude oils by thermocracking processes, for example, yield products of high sulfur contents as shown in Table 1.

Petroleum feedstock utilized in the U.S. is becoming increasingly heavier and higher in sulfur content as shown in Table 2. Consequently, refineries have to adapt to the use of heavier feedstocks (2). It is, therefore, imperative to establish future energy sources to meet our needs and to maintain and improve the U.S. economic competitiveness without compromising a cleaner environment.

Hydrotreating and hydrocracking processes are two conventional methods used to remove oil contaminants which consist mainly of compounds containing NSO heteroatoms and trace metals. Both processes use pressurized hydrogen gas with catalysts which convert the species of sulfur and nitrogen to H_2S and NH_3 respectively. These gaseous products are treated separately in subsequent processes. The catalysts used in both processes become gradually deactivated as the contaminants and trace metals start to deposit on their surface (4). Then fresh catalyst has to be brought in to make up for the loss of activity. Also, the deactivated catalysts have to be disposed as spent catalyst wastes. Both hydro-processes are expensive in terms of construction and operation costs (4). Moreover, these hydroprocesses together with other refining processes, e.g. distillation, thermal and catalytic cracking generate in an average plant tons of SOx, NOx, CO, hydrocarbons, waste waters, and solids emitted daily to the environment (5).

There are two approaches for processing the increasing heavier petroleum feedstocks into cleaner products. They are to either design a new refinery or to revamp the existing plants. Both options have considerable costs attached. In addition, new innovative methods will have to be explored and developed into cost-efficient and environmentally acceptable processes.

Contrary to conventional refining process conditions, biochemical treatment takes place at much lower temperatures and pressures. Significant R&D effort at Brookhaven National Laboratory (BNL) and elsewhere has shown that there are advantages in the application of several biochemical reactions in the treatment of fossil fuels (6,7,8,19). A demonstration plant for biological coal desulfurization is currently in operation (9). Biochemical petroleum desulfurization, denitrification and demetalization has been shown to be scientifically and technically feasible. Economic analysis indicates that the biochemical processing of petroleum is also cost-efficient (6,15).

MATERIALS AND EXPERIMENTAL

Details describing the preparation of biocatalysts, experimental procedures, chemical analyses, and instrumental protocols have been reported elsewhere (6,7,16,19). Any variation or modification in procedures that differ from the references cited is specified in the text.

RESULTS AND DISCUSSION

Organosulfur compounds found in petroleum oils can be classified as cyclic sulfides, thiophenes, disulfides, mercaptans, large polycyclics and polyaromatic sulfur compounds. (10,11). Most sulfur compounds are concentrated in heavy fractions of crudes with the highest concentration in fractions containing resins and asphalt (3).

Organonitrogen compounds in petroleum can be classified as basic and non-basic. The basic nitrogen compounds consist of pyridine types and are distributed in all boiling ranges. The non-basic nitrogen compounds include the pyrrole, indole, and carbazole types and are distributed mainly in higher boiling and residue fractions (3,13). Heteroatoms with an unshaired pair of electrons are capable of chelation formation of clathrates, charge transfer complexes, and coordination compounds. Such chemical structures contribute to the formation of three dimensional matrices, micelles, colloidal fluids, and molecular solutions which are characteristic of crude oils (14,16,6). Current evidence supports the view that the biocatalysts act at the heteroatom sites which leads to a breakdown of the three-dimensional structures and, in a manner of speaking, "depolymerize" the heavy crude (16).

In the development of biochemical processes for the upgrading of fossil fuels, it is important to retain most of the heating value of the fuels after treatment. This can be accomplished if the chosen biocatalysts are selective so that the processed fuels contain less heteroatoms and the biochemical treatment causes a minimum loss of

hydrocarbons. Thus the removal of sulfur, nitrogen, and trace metals and the conversion of heavy crudes to lighter oils is the main objective in the development of biochemical upgrading of heavy crude oils. Some of the recent results will be discussed in the following paragraphs.

Results shown in Figure 1, indicate that the biochemical desulfurization reactions take place in the lighter diesel as well as in the heavier fuel oil fractions of bunker oil. Comparison of this result with the corresponding gas chromatographic mass spectrometric (GC-MS) analysis in selective ion mode (m/e=57 for C4H9+) of untreated and treated samples (Fig. 2) indicated that the main hydrocarbons content of the treated sample was not significantly affected by the biotreatment.

Additional systematic chemical analysis of untreated and treated oils have shown that the oil/biocatalyst reactions depend on the chemistry of oils and a particular biocatalyst used (5,6,16,19). Some typical examples are given in Table 3. Several different types of heavy crudes and processed oils have been treated with different biochemical catalysts which yielded a range of products.

The GC-MS results of biochemical treatment of a steam recovered heavy crude, Midway Sunset (MWS) are shown in Figure 3. The chromatographic analysis indicates that a substantial amount of sulfur content has been reduced. In addition to sulfur, the organonitrogen content was reduced as well as shown in Table 3. Comparable analysis using three other oils, (MWS, Offshore California OSC, and bunker oil) are given in Figure 3. The results are different because the chemistries of the oils, MWS and OSC, are different from the refined petroleum products of Bunker oil. OSC is a heavy immature crude. MWS has been steam treated and the bunker oil is a distilled fraction, therefore, the chemical composition and history differs. In terms of heteroatoms such as nitrogen, for example, the lighter molecular weight heterocyclics would have been removed and larger molecules redistributed in favor of heavy fractions. In the case of OSC, the biocatalyst(s) are introduced in a sense into a "chemically" unaltered oil and, therefore, the biochemical effect is more apparent.

The chemistry of a feedstocks affects strongly the yield and the quality of the refined products. For example (Table 1), thermal cracking processes of vacuum residue feedstocks from four typical crude's yield products with sulfur contents which are directly related to the sulfur content of the feedstock used. Therefore, fuels derived from low grade high sulfur crudes are undesirable both in terms of process technology and environmental consequences. Further, the results from a typical hydrotreating process of feedstocks with increasing sulfur contents, e.g. naphtha, distillate and vacuum gas oil showed that the feedstocks with higher sulfur content require a six fold increase in the consumption of reagent hydrogen and the catalyst for the process (4). This results in an increase in the processing costs for hydrogen and to a lesser extent in the cost of consumed catalyst.

However in the case of the latter, the cost of spent catalyst disposal and its impact on the environment is significant (5).

The removal of vanadium and nickel by biochemical treatment, shown in Table 4, is of particular significance to refineries. These trace metals are known to affect the cracking and hydrotreating processes and also poison the catalysts used (4,14). The removal of these metals reduces operational costs and subsequent emissions to the environment.

A conceptual block diagram of a biochemical process is shown in Figure 4. The produced biocatalyst is mixed with a heavy crude feed in a biochemical reactor with a reaction time of 36 hours. The reaction mixture is separated in an oil water settler where the separated aqueous phase containing active biocatalyst(s) is recycled back to the bioreactor or sent to waste water treatment unit for recycling of water. The upgraded oil is separated and fed to an existing refinery stream.

An economic analysis based on the addition of a bioprocessing system to an existing refinery has shown that such a process is economically feasible (6,15). Assume that the plant is constructed with a loan at 10% annual interest rate and operated for a life span of ten years. During operation the plant desulfurizes a 3% weight sulfur heavy crude to a 2% weight sulfur lighter crude in 36 hours. For such an operation, the profit gain from the upgraded oil over the low price of heavy crude feedstock is sufficient to pay back the investment in eight years. Extended cost analysis has also shown that a higher desulfurization rate, lower loan interest rate and shorter reaction time make the process more profitable and reduce the pay-back time to less than two years (6).

The above economic analysis was based on price evaluation of the upgraded crude oil in terms of sulfur reduction only. In general, the market price of crude oils is related to the sulfur content. The lower sulfur oils have higher market value, therefore the value of desulfurization process can be evaluated. The whole biochemical process, however, also reduces nitrogen, metals, and improves lighter fraction yields. At present, these additional credits are hard to estimate, because refineries have their own formulas to determine the characteristics and values of their feedstock which are proprietary. Therefore, no market prices are available which explicitly relate to the nitrogen and metal contents in a manner comparable to that of sulfur. The additional credits may be calculated in an indirect manner such as tradable credits under the Clean Air Act (17).

CONCLUSIONS

Biochemical processes have been shown to be cost efficient and technically feasible in desulfurization, denitrification, demetalization and depolymerization of low grade heavy crude oils. When fully developed, they will be complimentary to the existing oil process technologies and simultaneously contribute in a cost-efficient manner to a better environment.

ACKNOWLEDGMENT

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REFERENCES

1. EIA, "EIA Forecasts World Oil Demand of 99 Million Barrels per Day in 2015," EIA New Releases, p. 3, Vol. 2/1996, DOE/EIA-0204 (96/2).

2. The U.S. Petroleum Industry past as Prologue 1970-1992, Energy Information Administration Office of Oil and Gas, U.S. Department of Energy, Washington, DC 20585, DOE/EIA-0572, p. 21, October 1, 1993.

3. Speight, J.G., "The Chemistry and Technology of Petroleum," New York, Marcel Dekker, Inc., 1991.

4. Cabrera, C.N., "UOP Hydrotreating Technology" in Handbook of Petroleum Refining Processes, p. 6-17 to 6-25, (Meyers, R.A. ed.) New York, Mc-Graw Hill Book Co., 1986.

5. Sittig, M., Petroleum Refining Industry Energy Saving and Environmental Control, Park Ridge, N.J.:Noyes Data Co., 1978.

6. Premuzic, E.T., Lin, M.S., Lian, H., Zhou, W.M., and Yablon, J., "The Use of Chemical Markers in the Evaluation of Crude Oil Bioconversion Products, Technology, and Economic Analysis," presented at the Fifth International Symposium on the Biological Processing of Fossil Fuels, Madrid, Spain, March 19-22, 1996.

7. Premuzic, E.T. and Lin, M.S., "Process for Producing Modified Microorganisms for Oil Treatment at High Temperature, Pressures, and Salinity," U.S. Patent No. 5,492,828 (1966).

8. Fedorak, P.M., "Microbial Metabolism of Organosulfur Compounds in Petroleum" in Geochemistry of Sulfur in Fossil Fuels (Orr, W.L. and White, C.M., eds.) American Chemical Society Symposium Series 429, 93-112. 1990.

9. "Porto Torres Pilot Plant," Proc. Fourth International Symposium on Bioprocessing of Fossil Fuels, Alghero, Italy, Sept. 1993.

10. Hunt, J.M., "Petroleum Geochemistry and Geology," San Francisco, W. H. Freeman & Co., 1979.

11. Strausz, O.P., Lown, E.M., and Payzant, J.D., "Isolation of Sulfur Compounds from Petroleum," in Geochemistry of Sulfur in Fossil Fuels (Orr, W.L. and White, C.M., ed.), ACS Symposium Series 429, 83-92 (1989).

12. Bakel, A.J. and Philip, R.P., "The Distribution and Quantitation of Organonitrogen Compounds in Crude Oils and Rock Pyrolysates," Adv. Org. Geochem. 16, 353-367, (1989).

13. Feintuch, H.M., Bonilla, J.A., and Godino, R.L., "FW Delayed Coking Process," p. 7-1 to 7-61, in Handbook of Petroleum Refining Processes (Meyers, R.A. ed.) New York, McGraw-Hill Book Co., 1986.

14. Yen, T.F., "The Role of Trace Metals in Petroleum," Ann Arbor, Mich., Ann Arbor Science Publishers Inc., 1975.

15. Dounias, G.A. and Stavropoulos, K.D., "Economics Feasibility of Biochemical Upgrading of Heavy Crudes," Final Report to BNL, 1995.

16. Premuzic, E.T., Lin, M.S. and Manowitz, B., "The Significance of Chemical Markers in the Bioprocessing of Fossil Fuels," Fuel Processing Technology 40, 227-239, (1994).

17. ES&T News, "EPA Gives Go-Ahead to VOCs/NOx Trading," Environmental Science & Technology Vol.29, 8, p. 355a (1995).

18. Knight, W.N.N. and Peniston-Bird, M.L. "Cracking and Reforming," p. 278-344, Modern Petroleum Technology, New York, John Wiley & Sons, 1973.

19. Lin, M.S., Premuzic, E.T., Yablon, J.H., and Zhou, W.M. "Biochemical Processing of Heavy Oils and Residuum," Applied Biochemistry and Biotechnology, p. 659-664, (1996).

Table 1.
Feedstock and Product Characteristics of Refining Processes

Process	Visbreaking	Delayed Coking		
Feedstock	Louisiana Residue	African Residue	Middle East Residue	Mexican Residue
TBP cut point, °C	480+	482+	538+	538+
Gravity, °API	11.8	12.8	8.2	4.0
Sulfur, wt %	0.61	0.6	3.4	5.3
Products				
Dry Gas and wt %	0.6	6.2	9.2	10.5
Naphtha, wt %	6.2	18.5	17.4	21.4
Gravity, °API	51.6	56.1	58.3	54.9
Sulfur, wt %	0.26	0.1	0.5	0.9
Gas Oil, wt %	6.3	65.3	48.5	33.0
Gravity, °API	46.5	22.4	25.3	20.5
Sulfur, wt %	0.33	0.59	2.28	4.26
Coke or Tar, wt %	87	10.0	24.9	35.1
Sulfur, wt %	0.58	1.1	5.1	6.4

ref. 13, 18

Table 2.
U.S. Utilization of Heavier, High Sulfur Crude Oil, 1981-1992

Year	Sulfur Percent by Weight	API Gravity (degrees)
1981	0.89	33.74
1982	0.91	33.11
1983	0.90	33.19
1984	0.94	32.96
1985	0.91	32.46
1986	0.96	32.33
1987	0.99	32.22
1988	1.04	31.93
1989	1.06	32.14
1990	1.10	31.86
1991	1.13	31.64
1992	1.16	31.32

Sources: Energy Information Administration, Petroleum Supply Annual, Vol. 1, 1991, Tables FE9 and 16, and 1992, Table 16.

Table 3.
Biochemical Treatment of MWS, OSC and Bunker Oil at 55°C

Biotreatment	% Oil Recovered	Elemental Analysis %				% Heteroelement Removal	
		C	H	N	S	N	S
Control MWS Oil untreated		86.45	10.99	0.79	1.00		
MWS treated with BNL 4-23	101	86.02	11.67	0.64	0.50	20	50
MWS treated with BNL 4-22	94	86.00	11.21	0.59	0.80	25	20
Control untreated OSC		82.31	11.17	0.66	4.40		
OSC treated with BNL 4-22	100	83.87	11.75	0.53	4.20	20	5
OSC treated with BNL 4-23	99	84.45	12.39	0.36	2.40	45	45
Control Bunker untreated		85.71	9.99	0.42	2.86		
Bunker treated with BNL 4-23	96	84.38	10.11	0.43	2.58	0	10
Bunker treated with BNL 4-22	95	84.00	10.06	0.40	2.33	5	20

Table 4.
Oil Metal Removal by Biotreatment

Element	Bunker oil untreated μ/g[a]	Bunker oil treated BNL 4-23 μg/g,[a], %[b]		Bunker oil treated BNL 4-22 μg/g,[a], %[b]		MWS untreated μg/g[a]	MWS treated BNL 4-23 μg/g,[a]%[b]		MWS treated BNL 4-22 ug/g, %	
Vanadium	5077	3076	40	4397	24	24	15	37	18.8	20
Nickel	627	344	45	513	19	63	47	25	52	18
Lead	22	22	0	21	2	2.9	2	30	0.14	95
Mercury	152	32	79	43	72	0.6	0	100	0.02	96
Zirconium	11	19	0	13	0	1.1	0.6	50	1.2	0
Silver	30	0	100	4	87	0.7	0.0	100	0.0	100
Molybdenum	13	0	100	7	46	0.7	0.1	85	0.2	72
Strontium	13	2	85	0	100	0.3	0.09	72	0.38	0
Selenium	0	0	NA	0	NA	0.04	0.0	100	0.0	100
Arsenic	0	0	NA	0	NA	0.51	0.01	98	0.06	88

[a] Metal content in oil samples as μg of metal/g of oil.
[b] Percentage metal removal by biotreatment in comparison to corresponding untreated samples.

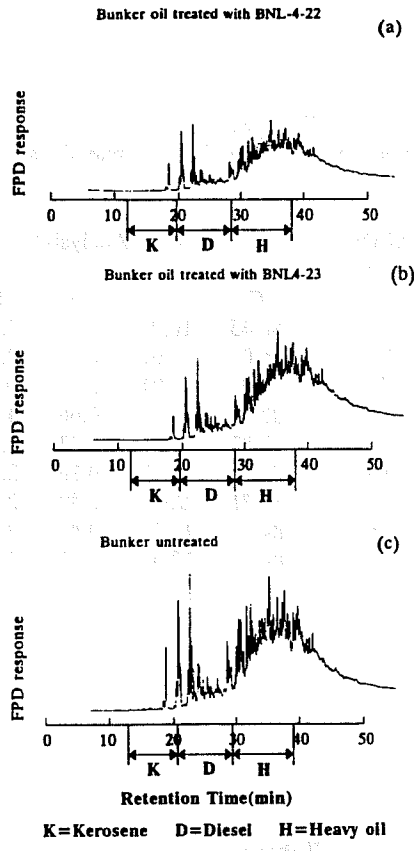


Figure 1. Sulfur specific trace (FPD) chromatogram of biochemical treated Bunker oil. (a) Bunker treated with BNL 4-22, (b) Bunker treated with BNL 4-23, (c) Bunker untreated

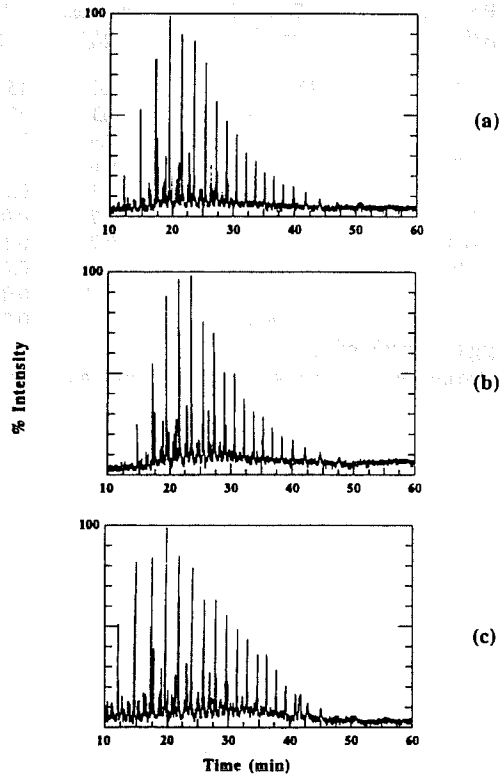


Figure 2. Gas chromatogram of Bunker oil M/e57 trace for hydrocarbons trace of (a) treated with BNL 4-22, (b) treated with BNL 4-23, (c) untreated

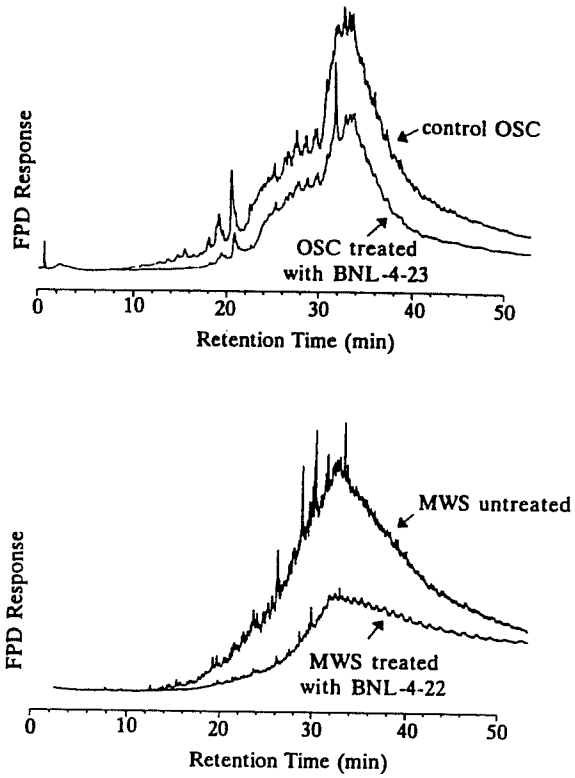


Figure 3. Gas chromatogram selective (FPD) analysis of OCS and MWS oil.

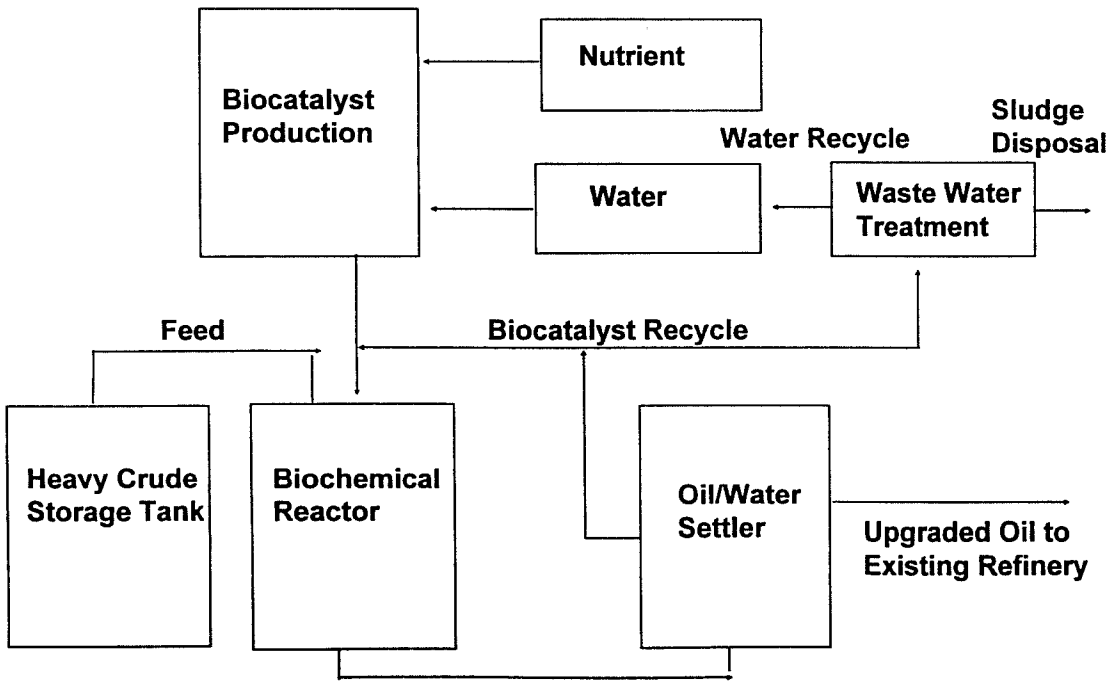
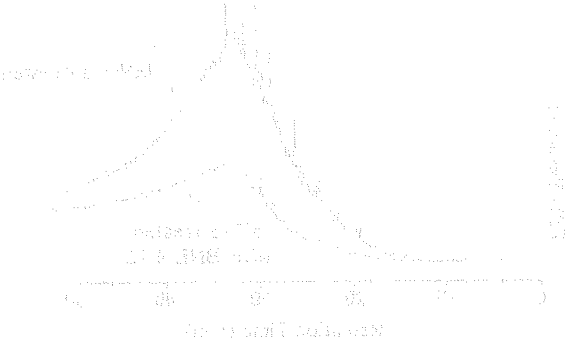
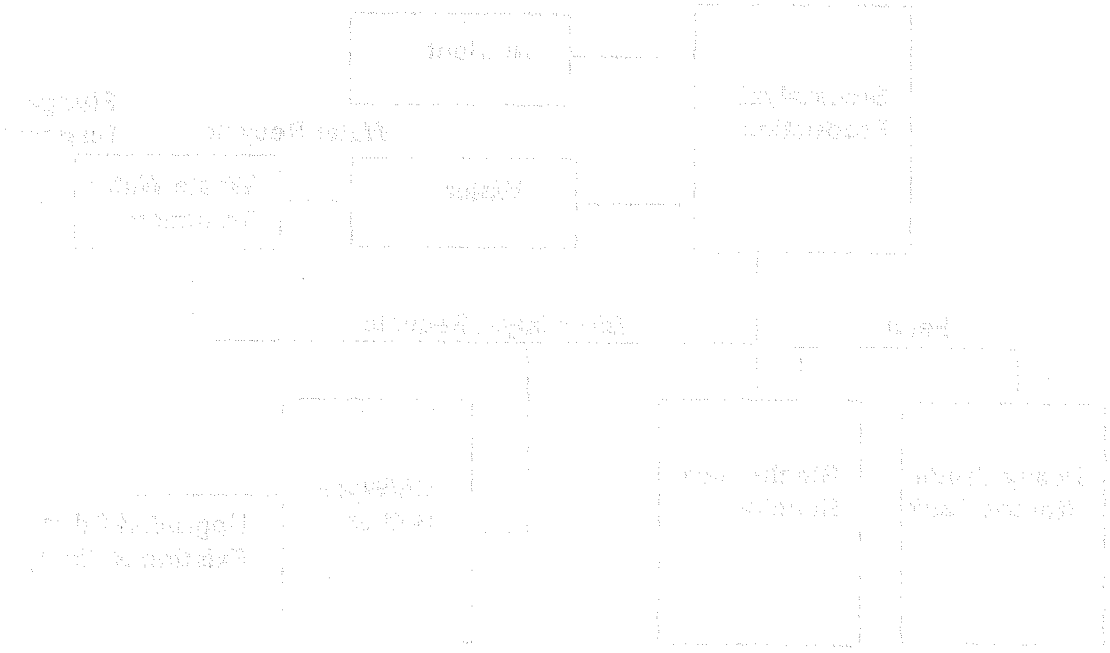


Figure 4. Block Diagram of Biochemical Process





Environmental Management, Compliance and Auditing

Practical Environmental Auditing

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I. INTRODUCTION

What is an environmental audit? At the risk of stating the obvious, an environmental audit is simply a structured evaluation of a company's compliance with environmental laws and regulations. If you don't trust our definition, the following is EPA's definition: "Environmental Audit" has the definition given to it in EPA's 1986 audit policy on environmental auditing, *i.e.*, "a systematic, documented, periodic and objective review by regulated entities of facility operations and practices related to meeting environmental requirements" 60 F. R. 66710 (12/22/95).

Both our definition and the EPA definition use as a benchmark the status of compliance with laws and regulations pertaining to public health and the environment. As anyone working with environmental issues is only too painfully aware, the number and complexity of these laws and regulations is mind-boggling. As noted by a leading environmental litigator.

"With the specter of administrative, civil and criminal penalties looming in the not-so-far distance in the event of a violation of the environmental laws, as well as the possibility of citizen suits and toxic tort lawsuits, the protection of an environmental self-audit is as important as ever. Faced with the myriad of penal possibilities, it is extremely important to know exactly how the environmental self-audit is being planned and conducted, what is going to be disclosed and how that information is going to be protected. The answers to those questions may cause you to gray prematurely."[1]

The purpose of this paper is to help you develop and effectively use an environmental audit to enhance the compliance of your company with environmental laws and regulations. The emphasis is placed on environmental

[1] James, Walter, D., Esq., Audits and Voluntarily Disclosure" presented to Independent Liquid Terminal Association, 16th Annual International Operating Conference, June 10, 1996.

audits and their approach as they apply to your company. Boiler plate environmental audits are at best a waste of time and money and at worst raise compliance issues that don't exist, while not giving due attention to the key compliance issues pertinent to your company.

II. PRIMER ON ENVIRONMENTAL AUDITS

If you do not currently have an environmental auditing program the threshold question is whether you need one. Very few businesses in the petroleum industry would not have some need for a limited environmental audit of their operations. Handling of chemicals in any fashion, disposal of chemicals, and any work performed around oil and gas is regulated under one or more federal or state environmental laws.

If you already have an environmental audit program in place, does it adequately protect you from liability? Many times, environmental audit programs do not have their origins in proactive compliance. Most company audit programs are developed in reaction to violation of a particular law, or initiated after an employee returns from a conference such as the one for which this paper will be presented. Remember, the worst environmental audit program is one which is not used. In other words, to have on file a historic audit program, with associated audit materials and findings and then to let the audit program lapse is substantially more egregious to a regulatory agency than good faith ignorance of the law. While ignorance of the law is no defense, it is certainly easier for a regulator to mitigate penalties in that scenario than it is to provide a penalty reduction for someone who had knowledge regarding potential violations of environmental laws and clearly chose to ignore them.

Another problem with many environmental audit programs is that they do not focus on appropriate problem areas. Many times, environmental audits take on a life of their own and focus on issues of interest to the individual conducting the audit. Another problem is the environmental audit documentation often lists a number of questions that are clearly not pertinent to your operations. Finally, many audits invite rambling narrative comments from the auditor, often resulting in statements which later could be damaging and create more liability issues than they solve.

As stated above, there are numerous federal and state laws and regulations that pertain to environmental matters. The statutes and regulations can be somewhat broken down by the type of chemical and what media is being exposed to said chemical. If your company does not come in contact with a certain media or use certain types of chemicals then ignore the laws pertaining to that media/chemical and exclude any reference to them in your audit materials.

A. SELECTED FEDERAL ENVIRONMENTAL LAWS

An example of how environmental laws may or may not apply to your operations is illustrated by the following hypothetical. Suppose you are an independent operator of several oil wells and associated storage facilities. You also operate a waterflood operation associated with several wells. Are your operations subject to the following federal environmental laws?

- Comprehensive Environmental Response, Compensation and Liability Act

  Sections: 42 U.S.C. §§ 9306, 9609, 9651-9659

Comment: CERCLA does not generally apply to pure petroleum products based on the CERCLA "petroleum exclusion" found at 42 U.S.C. § 9601 (14). However, CERCLA does apply to other chemicals which would be associated with oil field operations (solvents, etc.) and would also include petroleum products which have become contaminated and are considered "waste". Part of the key provisions under CERCLA for day-to-day oil field operations would concern any releases of waste petroleum products which would be considered hazardous substances and SARA Title III reporting requirements for any stored chemicals which would be considered hazardous substances.

- Resource, Conservation and Recovery Act

  Section: 42 U.S.C. § 6928 (d)

Comment: Any solid or hazardous wastes which are generated from oil field operations are potentially subject to RCRA disposal requirements. Further, groundwater and other types of similar contamination could subject operators to RCRA citizen suit claims.

- Clean Air Act

  Section: 42 U.S.C. § 7413 (c)

Comment: In general, the Clean Air Act may not apply to many small operators unless equipment such as compressors, dehydrators, heaters or other such stationary emissions-producing equipment is used. With regard to hazardous pollutant emissions, the Clear Air Act may eventually require even small operators who frequently use hazardous chemicals which are emitted into the air to file inventory documentation and control emissions.

- Clean Water Act

  Section: 33 U.S.C. § 1319 (c)

  Comment: The Clean Water Act, and its primarily marine environment companion known as the Oil Pollution Act of 1990, (33 U.S.C. §2701 *et seq.*) regulate discharges of pollutants and contaminants into navigable waterways. Discharges of oil field waste, including saltwater, into surface water bodies could be regulated under the Clean Water Act.

- Occupational Safety and Health Act

  Section: 29 U.S.C. § 666; 29 C.F.R. § 1926.59

  Comment: OSHA would apply to the handling of chemicals by employees. Particularly, OSHA requires certain levels of training for employees who are handling chemicals and may also impose additional liability on oil companies due to the OSHA multi-employee work site doctrine.

- Toxic Substance Control Act

  Section: 15 U.S.C. § 2615 (b)

  Comment: Of note to the oil and gas industry is the regulation of TSCA over PCBs. Particularly in gas condensate, PCBs come from sources such as greases used in lubricating valves and pipe fittings. Section 8 of TSCA also requires inventory of hazardous chemicals, which was the subject of recent litigation as it pertains to the oil and gas industry and disposal of gas condensate contaminated with PCBs and other toxic substances.

- Federal Insecticide, Fungicide, and Rodenticide Act

  Section: 7 U.S.C. § 1361 (b)

  Comment: Applications of herbicide on properties operated by oil producers for weed control may also be regulated under FIFRA. Particularly where herbicides or other pesticides are applied adjacent to surface water features.

B. STATE ENVIRONMENTAL LAWS

The laws of each state in which you do business should be surveyed to determine their applicability to your operations. Generally, the true

"environmental" laws of a given state mimic their federal counterparts. However, the key area of state regulation involves those laws specific to oil and gas exploration and production activities. Most states have a separate agency created solely for the purpose of regulating oil and gas production, along with unique laws and regulations *i.e.,* the Oklahoma Corporation Commission. For many of you, these are the laws and regulations which predominate your compliance benchmark. A dissertation on each state's "environmental" laws pertaining to oil and gas exploration and production activities is beyond the scope of this paper and we would encourage you to consult with in-house and outside counsel for state-specific advice.

C. PRIOR VIOLATIONS

Perhaps one of the best ways to determine what laws your environmental audit should focus on is to look at any past regulatory enforcement matter your company has been involved in. Have you been cited for improper disposal of saltwater, release of oil into surface water, failure of your employees to observe OSHA personal protection requirements, storage of regulated materials beyond pertinent deadlines, etc.? If so, then compliance with the environmental laws pertaining to these violations should be a primary focus of your audit. If your company has somehow managed to avoid even a minor enforcement violation, you are either very compliant or very lucky, and we suspect you fall into the latter category.

If you have only a few minor prior violations (or none) on which to focus your analysis of compliance with pertinent environmental laws, then we strongly suggest you quiz those with similar operations and attempt to find out what regulatory problems they have encountered. Many times, companies are reluctant to share audit checklists because they feel that it either identifies past violations or would be relied upon by other companies and, if not followed properly, cause them to incur liability. Such concerns can be alleviated by signing a simple confidentiality agreement related to audit checklists and release the author from liability due to reliance on the checklist questions.

III. REDEFINING YOUR AUDIT PROGRAM

Once you have determined the environmental issues associated with your operations and the area of law that apply to said operations, your current audit practices should be scrutinized. It is at this point you should strongly consider discarding any voluminous audit check-list (which has probably become the size of the telephone book). Instead, apply some common sense and develop an audit check list and audit program that is pertinent to <u>your</u> operations.

A. THE AUDIT CHECKLIST

If your company has an existing audit checklist, then it should be updated prior to each audit. If your company does not have an existing audit checklist it should develop one. Whether your company has an audit checklist or not, it is recommended that you attempt to share checklist questions with companies that are similarly situated to your operations. The following are other good sources of checklist information:

- State regulatory agencies;
- U.S. EPA (regional offices);
- Industry associations;
- Environmental consulting firms;
- Law firms.

There are several points to consider when compiling/revising your audit checklist. First, when creating or revising an audit checklist, remember that any information can and will be used against you. This is why the importance of limiting the questions or areas of observations on your audit checklist to those pertinent to your operations is so important. A thirty page audit checklist with only ten pages completed will come back to haunt you, should it later be learned you have a violation pertinent to an entry on your audit checklist which was overlooked because it was thought not to apply.

Second, make the form as close to a "true" audit checklist as possible. Questions should be answered in a "yes" or "no" format whenever possible. If "not applicable" is a permissible answer, then make the auditor explain in writing (with the following caveat) why.

Third, discourage lengthy narratives. You <u>are not</u> looking for a legal opinion from the auditor, you are instead looking for information on whether or not a particular activity is in compliance, out of compliance, or will certainly lead to non-compliance with pertinent environmental laws. Opinions, impressions, concerns, etc. are best left to discussions in the board room, less they be used against you in the courtroom.

Finally, remember those other audit forms you got from your acquaintances, friends at the EPA, etc. Once you have developed an audit checklist, our advice is to throw these away. Your audit files should contain only your audit reports and any associated correspondence/memoranda.

B. WHO SHOULD CONDUCT YOUR AUDIT?

We recommend that a limited number of in-house personnel be chosen to develop your audit program and revise your audit checklist, along with a limited outside support group. For example, if you are a small independent producer, then one employee with knowledge of your field operations will suffice. If you are a major oil company with diverse operations, then your environmental manager plus one representative from each pertinent business unit should form a competent in-house team. An outside consultant and legal counsel should be retained to refine and finalize the audit checklist.

Why hire a consultant or lawyer? A consultant is needed because this person/company will actually conduct the audit. Unless you are a major oil company with resources to have an internal auditing staff knowledgeable of environmental issues, your employee(s) is placed in an awkward and often in-effective role of auditing the very operations where his or her friends work and for which the auditor/employee may have responsibility over.

The outside counsel is needed to both interpret those laws that apply to your operations and to maintain a claim of privilege over any audit findings and follow-up correspondence. The outside counsel may also attend the actual audit, and will definitely be called upon to review the draft audit report.

The most important requirement in hiring an outside consultant and lawyer is previous experience. Make certain the individuals hired have a working knowledge of your operations or operations similar to yours. Make certain that these individuals have participated in other audits. Finally, make certain that the firms you hire use only those individuals you have selected to perform the work.

C. HOW SHOULD AN AUDIT BE CONDUCTED?

We would suggest that an audit be conducted in an unannounced fashion, with a goal of evaluating the real-time, day-to-day operations of your company. To avoid any negative feelings by your employees, it should be announced that your company has decided to institute periodic environmental audits. Your employees are then on general notice that an unannounced audit will occur sometime in the future.

With regard to when the audit should occur, absent any known compliance problems, the audit should focus on that period of time when violations could likely occur, focus on easily seen evidence that violations have taken place or are imminent, or examine for general signs of good operational practice.

It is instructive to examine such an audit policy with respect to state environmental regulation. For analysis purposes, we would offer the following example from the Oklahoma Administrative Code. In Oklahoma, for example, "tanks for drilling mud or deleterious substances used in the drilling, completion or re-completion of wells shall be constructed and maintained so as to prevent pollution of surface and subsurface fresh water" (OAC 165:10-3-13(a)). Proper audit of such facilities and activities should take place when they are active. It would not make any sense to audit empty tanks or pits for leakage -- audit them for leakage when they are in use. An engineering inspection of tanks for obvious damage and holes that would or could produce leaks should be conducted when the tanks are empty and prior to use. "To prevent loss of birds due to oil, all open top tanks containing oil on the surface (are to) be protected from access to birds" (OAC 165:10-3-13(b)). It would be appropriate to audit protective netting when it is in use. This would be especially true after events such as storms having high winds, which might damage bird netting.

"All wellhead connections, surface equipment, and tank batteries shall be maintained at all times so as to prevent leakage of oil, gas, saltwater, or other deleterious substances" (OAC 165:10-3-12). Certainly, in the normal course of operations, oilfield workers observe wellhead connections, surface equipment and tank batteries. For obvious reasons, current liquid leaks are easy to detect. Likewise, since leaks leave residual oil and saltwater (and/or their effects) on the ground, the existence of past leaks is easy to audit. This also leads the way to the good operational practice of cleaning up after oil and saltwater leaks. To properly audit for leakage, past leaks must be cleaned up. Otherwise, it will be impossible to accurately determine the frequency or magnitude of leakage. An environmental policy of prompt clean up also provides an added benefit of greater direct employee involvement and interest in environmental matters.

"Oil storage tanks shall be constructed so as to prevent leakage. Dikes or walls, where necessary, shall be constructed so as to prevent oil or deleterious substances from polluting surface and subsurface water" (OAC 165:10-3-29). Dikes and walls surrounding oil storage tanks are in constant use, but when should they be audited? Such structures are generally stable, but do degrade over time. It might, therefore, be appropriate to audit them during use on a regular (perhaps every two to five years) basis for erosion or other damage. This form of audit controls long term decay of these structures, but does not protect against either high risk conditions or failure of high risk structures. Failure of earthen berms are more likely after heavy rains, and older structures are more likely to fail than new structures. It may make more sense to audit these earthen structures based on their age and the severity of events which might induce failure; earthen berms might be audited after storms with a given severity. The audit trigger for older structures would be less severe than that for newer structures.

Instruct your employees they are to cooperate with the auditors and answer any questions posed to the best of their knowledge. Instruct your auditor to discourage answering any substantive questions from employees and to refrain from giving any information. The auditors should not conduct a debriefing session at the conclusion of the audit and should simply inform the employees that someone from within the company will provide information to them regarding the audit findings.

IV. MANAGING THE RESULTS OF YOUR AUDIT

The written results of your audit should initially be limited to the audit checklist. An in-person debriefing session with the auditors should be held as soon as possible. The debriefing session provides you an opportunity to immediately address any problems and may help the auditors in understanding observations made during the audit. The debriefing session is normally followed by a written audit report, which should clearly be marked as a "draft" along with "privileged and confidential" on each page. Many companies choose to not produce a comprehensive written report and instead develop one or several follow-up reports addressing the audit findings as they relate to specific areas of operation.

A. RESPONSE TO AUDIT FINDINGS

Perhaps more important than the findings of the environmental audit is how you respond to the findings. In general, the negative findings will document actual or eventual violations of environmental laws. The timeliness with which you respond to the violations and the mitigation measures you employ will often dictate whether and to what extent your company will incur a fine. Your response time may also be a key factor in mitigating the expense of cleanup.

On July 1, 1991, the U.S. Department of Justice ("DOJ") developed a guidance memorandum which focused on prosecutorial discretion in the context of learning, through self-reporting or otherwise that a company has violated environmental laws. The guidance, entitled "Factors and Decisions on Criminal Prosecutions for Environmental Violations in the Context of Significant Voluntary Compliance or Disclosure Efforts of the Violator (hereinafter, "Factors") was developed to inform the regulated community what the DOJ interprets as "good faith" compliance. [2]

[2] The Factors document what the regulated community has experienced in dealings with regulatory agencies for years; good faith compliance will be rewarded. The Factors state DOJ's policy in this regard as follows, "It is the policy of the Department of Justice to encourage self-auditing, self-policing and voluntary disclosure of environmental violations by the regulated community by indicating that these activities are viewed as mitigating factors in the department's exercise of criminal environmental enforcement discretion".

While many members of the petroleum industry may be more concerned about state enforcement proceedings and landowner lawsuits than DOJ actions, the Factors provide an excellent road map to use with audit findings. The Factors reviewed by DOJ in an enforcement action are as follows:

- Voluntary Disclosure-Did the violator make a voluntary, timely and complete disclosure of the matter which may represent a non-compliance situation. According to the Factors, a disclosure is not considered "voluntary" if it is already specifically required by law, regulation, or permit.

- Cooperation-DOJ considers the degree and timeliness of cooperation as a mitigating factor. Full and prompt cooperation is required, particularly in the form of willingness to make all relevant information available to government investigators.

- Preventative Measures of Compliance Programs-DOJ will look to whether the company already had in existence a regular environmental compliance program. The DOJ will pay particular attention to whether this program was used on a regular basis, the complexity of the program and the scope of the program. The DOJ pays particular attention to whether there was a "strong institutional policy to comply with all environmental requirements".

- Pervasiveness of Non-Compliance-The DOJ will also look to whether there is a history of non-compliance by the company who is currently being investigated. The DOJ will also consider the number and level of employees who participated in unlawful activities and the obvious or serious nature of the non-compliance.

- Internal Disciplinary Action-The DOJ will look to whether and to what extent internal disciplinary action was taken to make certain that the violations investigated will not occur in the future, and the history of disciplinary action related to any past violations.

- Subsequent Compliance Efforts-The DOJ will look carefully at the results of the non-compliant activity and whether the company instituted subsequent efforts to remedy the non-compliant situation and make certain it does not happen in the future.

1. REPORTING VIOLATIONS

Reporting violations is perhaps the most difficult problem associated with an audit. The first and most important question to be answered is whether a violation actually occurred. Environmental laws and regulations are difficult to interpret and reporting requirements within these laws are even more problematic. Legal counsel should be consulted to advise whether notification is necessary and the time frame for compliant notification.

A number of states have recently added laws pertaining to disclosure of environmental audit findings and self-reporting. These laws often provide a statutory privilege related to disclosure of information to regulatory agencies and a bar against prosecution to those companies which voluntarily disclose, institute remedial measures and otherwise mitigate any harm caused. These laws have met with substantial resistance from EPA and it is currently unsettled as to how the conflict between EPA and the states regarding audit privilege laws will be resolved. As referenced above, the EPA recently published in the Federal Register at 60 F. R. 66706 (12/22/95) a policy entitled "Incentives for Self-Policing: Discovery, Disclosure, Correction and Prevention of Violations".

Discussion of the EPA Audit Disclosure Policy is beyond the scope of this paper. However, the following factors considered by EPA in mitigating any fines due to prompt disclosure are instructive:

- Was the discovery voluntary and not through a legally mandated monitoring or sampling requirement prescribed by statute, regulation, etc.

- Was the disclosure prompt *i.e.,* within ten days after the violation was discovered?

- Was the violation disclosed prior to commencement of a federal, state or local inspection, investigation or action?

- Was the violation corrected within sixty days or were efforts to remediate the violation instituted within a reasonable timeframe?

- Was the violation that occurred one which had occurred previously within the past three years of operation or otherwise a part of a pattern of similar consistent violations?

- Could the violation also result in other violations such as serious actual harm or endangerment to human health or the environment or otherwise violate specific terms of a judicial or administrative order, etc.?

- Did the violator cooperate with EPA and provide all information requested?

If notification is required, the actual notification should come in the form of a letter from the person in your company who can answer any questions posed by the regulatory agency regarding the violation. This letter should be sent certified mail return receipt requested in order to document that notification occurred.

Reporting a violation should be done in a positive fashion and <u>must</u> document the mitigation measures taken. If the violation is a release to the environment <u>do not</u> speculate as to the result of the release. For example, if a

tank of gas condensate spilled into a stream, you could report the following and generally comply with necessary reporting requirements:

- What was released;
- How the release was discovered (by whom);
- Time and date if known/location;
- Regulatory personnel contacted and how contacted;
- Spill containment and cleanup measures taken;
- Steps taken to ensure a similar release does not occur in the future.

An example of a common violation disclosed during an audit is where a drum of regulated waste has remained on site beyond the scheduled disposal date. The following information should be considered for inclusion in a notification letter regarding such storage violation:

- Time and date in which the violation was discovered;
- The circumstances behind the discovery that the time frame for disposal had been exceeded;
- Whether the waste was promptly sent off site and who managed the waste for disposal;
- Steps taken to ensure a similar violation does not occur in the future.

The key point is that where a violation requiring reporting has occurred, the reporting should take place voluntarily and as soon as possible. Further, all pertinent information reasonably available should be included. Prompt and good faith mitigation measures should also be reported.

V. COMPLIANCE PROGRAMS

Environmental audits are but one component of an overall company program to prevent and detect violations of environmental laws. Corporate compliance programs are the subject of numerous articles and commentary as a result of federal criminal sentencing guidelines. In general, the sentencing guidelines provide courts with the parameters to consider in imposing sentences and fines on criminal defendants. For many violations, the range of fines is based

upon the degree of egregious behavior shown by the defendant. In other words, if good faith attempt at complying with the law was made and the violation is an oversight, fines will be minimal to non-existent verses those who knowingly violate a given law. While the guidelines state nothing new, the substantial commentary from the guidelines regarding factors to be considered in mitigation of fines to be imposed provide the regulatory community with valuable information on what factors the court will consider as evidencing good faith attempts at compliance.

A detailed discussion of the sentencing guidelines and development of compliance programs is beyond the scope of this paper. We would however note that the guidelines, like the DOJ Factors discussed above, have come to be used by federal, state and local regulators as guidance for determining the severity of penalties to impose on a company for violating environmental laws. The following is an abbreviated list of information contained within the guidelines which federal prosecutors and courts look to in determining the severity of the sentence to be imposed:

- Did the organization appoint a high level executive (i.e., a compliance officer) to oversee compliance with the law.

- Did the organization delegate authority to individuals who the organization knew or should know have a propensity to break the law.

- Did the organization establish compliance standards and procedures (Compliance Manuals, etc.) that are required to be followed by employees **and agents** and are reasonably likely to prevent **and detect** violations of the law.

- Did the organization take steps to effectively communicate standards and procedures to employees and agents through training and/or other means (brochures, etc. distributed).

- Did the organization put in place monitoring and auditing systems to ensure compliance program is working (may include a hotline).

- Did the organization enforce violations of the compliance and procedures standards through appropriate discipline (type of discipline in case specific).

- If an offense is detected, did the organization take mitigation/remedial measures to ensure a violation does not happen again.

- Did the organization self-report (self-reporting is critical to receiving favorable review by prosecutor).

VI. CONCLUSION

As many companies in the petroleum industry have learned, good faith and proactive compliance with environmental laws and regulations generate substantial good will and ultimately results in substantial cost savings. A focused and updated environmental audit program clearly serves as a cornerstone in complying with environmental laws and regulations that are pertinent to your company's operations. The key to developing and maintaining an audit program that serves your company's needs is to continually refine and focus the audit program on those areas of your operations which would most frequently result in compliance problems.

Public Exhibitions: An Added Bonus of Cultural Resource Management Projects

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Cultural resource management (CRM) projects are often troublesome for proponents of construction projects. Federal laws and regulations that govern CRM require qualified consultants to help a project proponent navigate government mandates. Eligibility for the National Register of Historic Places (NRHP) is a standard for what is to be done with any cultural resources that are encountered and will be affected by the proposed project. Mitigation can vary with the type of site and the proposed undertaking. A part of the mitigation can be public interpretation. Even when it is not explicitly incorporated into a treatment plan, such public interpretation is a good investment and a small portion of the entire budget for archaeological work required by law. Returning information to the public invariably gains a company good will among its neighbors, and there are many potential spin-offs. There are a variety of directions, levels of effort, and forms that such public interpretation can take.

One of the most misunderstood aspects of environmental laws and regulations that project proponents face is cultural resource management or CRM. Unlike air or water quality issues, cultural resources are evaluated on a qualitative rather than quantitative basis. Significance is measured by standards which seem arcane, even arbitrary, to non-specialists in archaeology, history, or architectural history. Among the misunderstandings is the belief that a treatment plan proposed for one site can be used for all sites within a project area, that sites from the twentieth century are never significant, or that there is no acceptable alternative to avoiding a site or cancelling a proposed project. Unanticipated delays are the special bane of project managers facing CRM work.

In our presentation today we hope to clarify some of the complexities of cultural resources, suggest how to avoid unnecessary delays often resulting from CRM work, and propose how projects that are mandated by law can yield valuable, cost-effective interpretive exhibits with public relations benefits. First, we will discuss the types of historic properties affected by the requirements of legislation. Next, we will discuss CRM laws, regulations, and processes. Then we will consider types of mitigation. Finally, we will address how interpretation can be used as a part of mitigation and the positive public relations benefits that can be accrued as a result.

HISTORIC PROPERTIES

When laws and regulations discuss historic properties they include a wide range of sites and property types. Among them are: prehistoric camps, used for short periods by Indians who were hunting and gathering; large prehistoric villages built by Indians who grew corn and other crops, including the prehistoric ruins of the Southwest and the mounds of the Mississippi Valley; Colonial-period settlements, like the English fort recently uncovered at Jamestown, Virginia, or Spanish missions from Texas to California; major historic locations like Mount Vernon or Independence Hall; engineering and architectural masterpieces, like the Brooklyn Bridge and the work of Frank Lloyd Wright; examples of vernacular architecture, such as the houses of the people who never became famous but built this country; and landscapes, such as battlefields, city parks, and planned communities. Categories of historic properties include buildings, which housed people; structures, which served other functions; objects; sites, or locations; and districts, which contain multiple properties that have some common link that makes them significant as a group even though the individual elements may lack significance by themselves.

Each type of historic property is protected by the laws, but the measure of their significance varies. For instance, a surface scatter of stone tool-making debris left by prehistoric people will be treated in a way different from that applied to a standing historic structure.

THE LAWS AND PROCESSES OF CRM

The foundation of CRM is the National Historic Preservation Act (NHPA) of 1966, as amended. There were earlier acts of Congress and by the states, but this law, particularly Section 106, moved archaeology and historic preservation to the forefront of environmental concerns. In this law, Congress declared that: "the spirit and direction of the Nation are founded upon and reflected in its historic heritage; the historical and cultural foundations of the Nation should be preserved as a living part of our community life and development in order to give a sense of orientation to the American people; this heritage is being lost or substantially altered; preservation of this heritage is in the public interest; and that, although the major burdens of historic preservation have been borne by private agencies and individuals, the Federal Government must accelerate its historic preservation programs and activities to give maximum encouragement to agencies and individuals undertaking preservation by private means" (16 U.S.C. 470).

The act established the National Register of Historic Places (NRHP), a listing of important historic and prehistoric cultural properties, the State Historic Preservation Programs, the position of State Historic Preservation Officer (SHPO), and the Advisory Council on Historic Preservation (ACHP). The ACHP is an independent Federal agency that advises the President, Congress, and Federal agencies on historic preservation matters and arbitrates disputes over CRM decisions.

Section 106 of the NHPA is reactive in that it requires an agency to "take into account" how an undertaking could affect significant cultural resources and to provide the ACHP a reasonable opportunity to comment. An undertaking means a project, activity, or program funded in whole or in part under the direct or indirect jurisdiction of a Federal agency, including those carried out by or on behalf of the agency, those carried out with Federal financial assistance, those requiring a Federal permit, license, or approval, and those subject to state or local regulation administered pursuant to a delegation or approval by a Federal agency.

Generally, the Section 106 process may be considered a series of five steps:

1) Agency identification and evaluation of potentially significant historic properties;
2) Agency and SHPO consultation regarding assessment of potential effects of a proposed undertaking on historic properties;
3) Consultation between the agency and the SHPO in development of a treatment or mitigation plan;
4) Opportunity for ACHP comment; and
5) Proceeding with undertaking in compliance with terms of any agreement reached.

Identifying what are loosely called cultural resources (this is not a term defined by law) and determining their eligibility for the NRHP is an essential and mandated stage of the historic preservation process. Criteria for inclusion in the NRHP are as follows:

Criterion (a) Association with important events;
Criterion (b) Association with persons of historic significance;

Criterion (c) Possessing characteristic qualities of design or the work of a master; and
Criterion (d) Possessing the potential to yield data that can contribute to our understanding of the past.

Often archaeological sites are determined eligible on the basis of Criterion (d). Contexts deemed important by SHPOs and State Archaeologists are the basis for determining significance of archaeological sites. Historic properties such as standing structures, objects, or landscapes may also be eligible under Criterion (d), but most often would be eligible under Criteria (a), (b), or (c). It is important to understand that a cultural resource does not have to be listed on the NRHP to gain protection under the law. If a Federal agency and SHPO agree that a site is eligible for inclusion, it is protected under the law whether or not it is ever listed.

There are some limitations on what properties are eligible for the NRHP. For instance, the following are not eligible, except as part of a district or if it meets conditions outlined in what are called the criteria considerations: religious properties, buildings that have been moved, birthplaces and graves of important persons, cemeteries, reconstructed buildings, commemorative structures, and properties less than 50 years old. For most projects, the most important criteria consideration addresses the last instance. Although 50 years is the minimum age for inclusion in the NRHP, there is an exception for properties that have achieved significance of exceptional importance more recently.

Should sites be destroyed as a result of agency undertakings without completion of the Section 106 process, the agency is required to inform the SHPO and the ACHP in writing as to what happened and why. Technically, the ACHP can sue a Federal agency for noncompliance, although this does not normally happen. More likely are lawsuits brought about by interested parties involved in the Section 106 process, which could include but are not limited to the SHPO, the State, Native American tribes, or any individual or group of individuals concerned with the proper management of cultural resources.

Whereas NHPA requires that cultural resources be "taken into account", the Archaeological Resources Protection Act (ARPA) of 1979 as amended, is considerably more severe in the penalties it can enact. ARPA provides for civil and criminal penalties to be levied against those who would willfully or otherwise destroy cultural resources. Both felony and misdemeanor sanctions may be applied to persons who violate ARPA prohibited activities. Under ARPA:

- No person may excavate, remove, damage, or otherwise alter or deface or attempt to excavate, remove, damage, or otherwise alter or deface any archaeological resource located on public lands or Indian lands without a permit.

- No person may sell, purchase, exchange, transport, receive, or offer to sell, purchase, or exchange any archaeological resource in violation of ARPA or any other Federal law.

- No person may sell, purchase, exchange, transport, receive, or offer to sell, purchase, or exchange, in interstate or foreign commerce, any archaeological resource excavated, removed, sold, purchased, exchanged, transported, or received in violation of any provision, rule, regulation, ordinance, or permit in effect under state or local law.

- Any person who knowingly violates, or counsels, procures, solicits, or employs any other person to violate, any prohibition contained in subsection (a), (b), or (c), shall be held accountable under the law.

ARPA violations can also be prosecuted through a civil process. Civil proceedings are pursued in administrative law courts initiated by the appropriate Federal land manager. Civil proceedings are analogous to damage assessments performed by Federal agencies in that damage assessments are billed to the perpetrator. The advantage of civil prosecution under ARPA is that the government's burden of proof in a civil case is considerably less than in a criminal case, thus increasing the likelihood of conviction.

ARPA also provides for a permitting process for the lawful excavation of archaeological sites. Unlike the first historic preservation law in this country, the Antiquities Act of 1906, ARPA provides uniform guidance for the issuance of such permits requiring that the applicant be qualified, that research designs and mitigation plans are credible, that a specified level of work will be accomplished within a specified period of time, and that the resources removed will remain the property of the United States. ARPA also stipulates that Indian tribes having a religious or cultural interest in an archaeological site on public land must be notified 30 days before an excavation permit is issued. It is the prerogative of tribal officials to comment upon the issuance of the permit, and the land manager may stipulate mitigation measures in permit requirements. The opportunity for interested parties to comment is just one major reason that planning for cultural resources compliance be initiated early in the life of an undertaking.

MITIGATION

In consulting for project proponents, archaeologists and other cultural resource specialists must know the laws and the process by which they are enacted, the cultural history of the project area, and the concerns of state and Federal regulators regarding research issues. Not adequately doing research or doing research at the latest possible moment in a project, invites unforeseen delays resulting in great potential costs.

Typically there are three steps to archaeological cultural resources investigations undertaken by contractors specifically designed to comply with NHPA and ARPA. The first of these is survey: i.e., finding sites. This step normally includes site file searches to determine which sites have been previously recorded in a given area and actual field inventory to locate and record previously undocumented sites. The survey report, which summarizes the results of survey, normally includes eligibility recommendations that are consulted on by the agency and

SHPO. Sometimes, however, determination is not possible at the survey level. In the event that site eligibility remains undetermined, sites that appear to have the potential to qualify for the NRHP are subjected to site testing; the result of testing is learning more about the sites, as well as a definitive determination of NRHP eligibility. The third phase, data recovery, is discussed below.

It should be emphasized that a determination of eligibility for the NRHP does not mean that an undertaking cannot proceed. Project proponents who follow the CRM process, have an experienced consultant, and begin early enough in the project will avoid difficulties. They will have a range of options. One is redesign to avoid NRHP eligible properties. Another is data recovery, the third stage of the CRM process. Data recovery is a thorough, well-planned research effort aimed at extracting the most possible information from a site that will be altered by the proposed undertaking. It is also known as mitigation because it preserves a site's information potential in archival form.

Some latitude exists in deciding whether data recovery is the best form of mitigation. Archaeological sites, which are usually nominated to the NRHP on the basis of Criterion (d) for their potential to contribute data on the past, are often mitigated through data recovery. Sites nominated on the basis of other criteria, such as (a), an association with a prominent person, are mitigated in other ways. The SHPO officers of some states are open to including public interpretation as an aspect of the treatment plan agreed upon in some cases.

Public interpretation fulfills an important aspect of the original intent of the NRHP because it brings the science to the people and people have a hunger to understand their past. In the words of NHPA, it preserves the historical and cultural foundations of the Nation "as a living part of our community life and development in order to give a sense of orientation to the American people" (NHPA 1966).

PUBLIC INTERPRETATION

A benefit of public interpretation is that an excellent public relations bonus can be realized by the project proponent. By public interpretation we mean popular reports and exhibits that bring the results of research to an intelligent but non-specialized reader. Our focus today is on exhibits, which have a much wider appeal and greater impact than popular reports.

Among the most successful exhibits we have planned, designed and installed is here in Albuquerque, at the Albuquerque International Sunport. Since it can be seen by conference participants, we will use it as our principal example of the bonus that can follow from cultural resources data recovery projects. Other projects for which public interpretation was or is about to be conducted include mining operations, a pipeline, and construction of a restaurant complex.

The Albuquerque International Sunport planned to expand a runway. Two prehistoric archaeological sites, one dating from about 800 B.C. and another from A.D. 1250, were found.

Investigation suggested that these were significant sites and clearly eligible for the NRHP. Without causing a delay in construction schedules, data recovery began in January 1995, continuing through a light snowstorm. A major site report was completed, and the project proceeded. What made this data recovery different from others is that the results were returned to the public, who ultimately pay for data recovery efforts, and the Airport gained positive publicity. The managers received credit for their efforts at CRM.

Guiding the public interpretation at the Albuquerque Airport is the principal that every place has a story. Even though the story is not as dramatic as a major battlefield or as visible as a large ancient ruin like Mesa Verde, the importance of what happened in a location is unique and provide a sense of place. Current trends in museums and museum education have taken up this theme, finding material to interpret not just in a grand setting but also in everyday locations; public interpretation of CRM projects for industry can use the same approach.

What lessons can be passed on from the Albuquerque airport exhibit? The following points in our experience may be useful to you.

1) There is a relatively small cost to turn archaeological work mandated by law into a positive benefit for project proponents.
2) Whereas archaeological clearance is the primary goal of CRM work, public interpretation is longer lasting, providing credit to project proponents for their compliance with environmental laws.
3) There is a wide range of options for cost, presentation, and format for public interpretation. The same materials derived from the mandated reports and curation of artifacts can be used for an exhibit; a brochure; a popular document; a CD-ROM; or school curriculum development; corporate newsletters; and business journals. The news media can also be supplied at a low additional cost, thereby expanding the exposure a business can get for the CRM project it has already funded.
4) Public interpretation is well received by SHPOs and agency regulators; it creates very positive feelings resulting in an improved working relationship. The benefits of being perceived as a corporate good neighbor cannot be underestimated. Our experience has shown that clients who engaged in public interpretation have reaped enormous good will from abuttors and local residents. Showing off the results of compliance pays off in many demonstrable ways.
5) Finally, public interpretation provides a service to the community in which a project is planned. Every place has a story, and public interpretation that tells the story is appreciated by neighbors of your project. Each project can have a theme developed to present the culture history, process of archaeology, and the contribution of the project proponent. In the case of the Albuquerque Airport, the theme of travelling through time was used to frame the data acquired through the mandated archaeological research for presentation to the public.

In summation, the law requires a process of consultation on historic preservation when Federal money, land, or permits are involved in a proposed project. There are ways to avoid unexpected delays through a timely use of qualified consultants in archaeology, history, and architectural history. Mitigation can vary with the type of site and the proposed undertaking. A part of the mitigation can be public interpretation. Even when it is not explicitly incorporated into a treatment plan, such public interpretation is a reasonable investment in getting a reputation as a good corporate neighbor since it takes only a small portion of the entire budget for archaeological work required by law.

Managing Environmental Regulatory Compliance Using an Online System

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ABSTRACT

An online hypertext environmental regulations manager for the petroleum industry has been created for the petroleum engineer. With the growing need for an understanding of environmental regulations, the hypertext system is designed to store environmental information and regulations and present them in an interactive and intuitive manner. This research will demonstrate the advantages of an on-line system to provide the unfamiliar engineer a logical methodology to comprehend the environmental aspect of the petroleum industry. Environmental operating guidelines are easily accessed by using a point and click method. The environmental guidelines recommended by the Oil Conservation Division (OCD), the regulatory agency for the petroleum industry in New Mexico, are presented as the primary focus of this work. These guidelines are categorized by five subject areas most useful to the petroleum engineer: drilling, production, pipeline and abandonment operations, and leaks, spill and release response. The manager also supplies the permitting requirements and procedures for environmentally sensitive operations such as drilling, injection and enhanced recovery and abandonment operations referenced to the OCD general operating rules and regulations for oil and gas exploration and production. The permitting procedures section also presents the necessary forms to be filed for such operations. Written in HTML (HyperText Markup Language), the manager is read using a browser such as Netscape Navigator. With the hypertext format, the program also furnishes Internet links to environmental information and resources like the EPA and the United States Congressional federal regulations in addition to commercial environmental World Wide Web sites. With the implementation of the regulations manager, the engineer has a new tool to work more efficiently, saving time and money. This system can be expanded to include not only environmental but all operating regulations for any state or country and is an effective method for future electronic filing of regulatory forms.

INTRODUCTION

Today, the Internet, the global connection of computer networks, is growing at an exponential rate creating a world-wide medium for the exchange of information. The petroleum industry is now taking advantage of this medium in the way of technology transfer. Technology transfer is just beginning to expand its capabilities as seen in the Gas and Oil Technology Exchange and Communication Highway (GOTECH)[1] information server. Technology transfer provides a new means to study areas of the petroleum industry previously not addressed such as environmental regulatory compliance.

The objective of this research was to develop a new method for the petroleum engineer to understand the environmental regulation aspect of oil and gas exploration and production without having to decipher volumes of reference materials. In the state of New Mexico, many agencies, aside from the Environmental Protection Agency (EPA), have strict environmental rules regarding oil and gas exploration and production. These agencies include the Bureau of Land Management (BLM), the Bureau of Indian Affairs (BIA), the Water Quality Control Commission (WQCC), the New Mexico Environment Department (NMED) and individual Indian tribes and pueblos. The primary governing agency for exploration and production is the New Mexico Oil Conservation Division (OCD). The OCD rules and regulations are the main focus of this work.

There have been many software programs designed to assist the petroleum engineer but not one which provides an overview of general information regarding the environmental regulation compliance area. The manager provides a unique organization of public data which are the rules and regulations of the OCD. These environmental rules are written for two main areas: water quality control and air quality control. A key feature of the manager is the organization of these rules and regulations into categories useful to the petroleum engineer such as drilling, production, pipeline and abandonment operations and leaks, spills and releases.

With the development of the Internet and World Wide Web, the new concept of hypermedia technology was introduced. Hypermedia incorporates information in an enriched environment that complements text with pictures, graphics, video and sound. Use of hypermedia allows the reader to quickly browse through linked, cross-referenced and layered information in a non-sequential manner. Hypertext[2] used in this research is one branch of hypermedia that deals mainly with text and graphics. One of the first examples of using this technology to present technical information is seen in NASA's "Development of an Intelligent Hypertext Manual for the Space Shuttle Hazardous Gas Detection System."[3]

In the petroleum industry, the applications of hypermedia are just beginning to be seen as in the GOTECH[1] server. Hypermedia, a new resource for presenting technical information, has yet to be utilized to its fullest extent and provides an excellent medium for presenting environmental regulations and guidelines

information. This methodology of organizing and presenting technical information can be expanded to include all rules and regulations pertaining to the petroleum industry such as proration practices and field rules and to regulations of other governing bodies as well. This methodology should also apply to similar types of technical information such as the American Petroleum Institute standards. The following will address the framework of this research along with a description of the software program's development, its capabilities and benefits.

SOFTWARE DEVELOPMENT

To provide some insight on how the technology used in this research was developed, it is necessary to answer the question "What is the Internet and the World Wide Web?"

The Internet. The Internet first started in the late 1960's as a research project of the Defense Advanced Research Projects Agency (DARPA). The United States Army, Navy and Air Force all had acquired computer systems each designed by a different vendor. The DARPA project was to develop a method for different computers to communicate with each other. Thus, ARPANET was created linking four research institutes: UCLA, Stanford Research Institute, UC Santa Barbara, and University of Utah in Salt Lake City. From this project, a set of standards were developed for computer systems to "talk" to each other known as TCP/IP (Transmission Control Protocol/Internet Protocol). Certain abilities of this network included file transfer, electronic mail and remote logon access. By 1971, ARPANET had expanded to 19 nodes including many other universities[4] outside the original four.

The National Science Foundation (NSF) began adding funding to the project in the mid-1980's to expand connectivity. NASA, the Department of Defense, and the Department of Energy also contributed funding and ARPANET developed into NSFNET becoming the framework the Internet. Initially connecting research centers along with college and university campuses and government agencies, the growth of the NSFNET along with the use of high speed data transfer ultimately attracted the attention of private industry. From then on the growth of the Internet, which actually describes the computer hardware and millions of miles of cable, has been exponential.

The World Wide Web (WWW). For the last 50 years, scientists have envisioned a universal information database. Such a database would be available to people around the world, but also the "information would link easily to other pieces of information so that only the most important data would be quickly found by the user."[5] Using today's technology, the Internet has finally provided the means to create this global database. Officially, the WWW is described as a "wide-area hypermedia information retrieval initiative aiming to give universal access to a large universe of documents."[5]

The Web began as a project at CERN (Conseil Europeen pour la Recherche Nucleaire) which is the European Laboratory for Particle Physics.

Although located in Switzerland, researchers from all over the world collaborate on many projects. Consequently, Tim Berners-Lee, a researcher at CERN, proposed the WWW project to create an effective means of transferring research and ideas throughout CERN. Soon after CERN's original proposal, the National Center for Supercomputing Applications (NCSA), located at the University of Illinois at Urbana-Champaign, started a project to create an interface for the World Wide Web. Based on hypertext, NCSA developed one of the first Web interfaces known as Mosaic, which was first distributed to the Internet community in 1993[6]. Mosaic included a standard format for identifying documents and their location or "address" on the Web know as a URL (Uniform Resource Locator).

HTML. HTML is the language in which information on the Web is written and provides the method for users to interact. The most unique feature of hypertext is that it contains connections, called links, within the text which lead to other relevant information. Hypertext uses codes called tags within the document to instruct the computer displaying the text on how to do so, including style and size of font. This is much like the earlier versions of WordPerfect, before the WYSIWYG (What You See Is What You Get) concept.

Netscape Navigator™ Netscape Navigator™ is a network browser that allows retrieval and viewing of World Wide Web hypermedia documents. The World Wide Web framework is based upon the client-server concept. A person uses a software program (the client) to connect to a remote computer system (the server), where information is stored that the computer user wants to access. Clients such as Netscape are also known as "browsers" and present the data in a hypertext format.

SOFTWARE DESCRIPTION

Now that some background has been provided about the techniques used to develop the program, the environmental regulations program's features and capabilities will be presented. Once the environmental regulations manager is accessed, the first screen the user sees is the homepage. This homepage provides an introduction to the program and a list of menu options, which may be seen in **Figure 1.**

Oil Conservation Division. After the introduction, the first section of the homepage provides information about the New Mexico Oil Conservation Division (OCD). The OCD is the primary regulatory agency for the petroleum industry in the state of New Mexico. The user can select links to the following information:

1. Overview of OCD Environmental Regulatory Programs
2. OCD Function Chart
3. OCD Personnel Organization Chart
4. Delegation of Authority for Oilfield Exploration & Production Operations
5. Water Quality Control Commission
6. OCD Telephone Directory

7. Map of OCD District Offices.

This gives the reader an overview of how the OCD began, its responsibilities, and its authority. The next section of the homepage provides a menu with five options for the engineer to choose, which include:

•Drilling Operations
•Production Operations
•Pipeline Operations
•Abandonment Operations
•Leaks, Spills and Releases.

Drilling Operations. Once the user selects this option, two more choices are given: 1) Permitting to Drill and 2) EPA Waste Classification for Oil and Gas Exploration and Production Wastes. The first option gives permitting procedures for a single well completion, a multiple well completion, and a bradenhead gas well completion. Permitting procedures include information on the forms that are required to be filled out, where to file the forms, and how many copies are required (**Figure 2**). Each form required in the procedure is highlighted along with the corresponding OCD rule. There are two ways a user can access these forms. First, click on a form, such as Form C-101: Application for Permit to Drill, and the computer will load up Microsoft Word™. The user will see the form within Microsoft Word™ and then be able to fill it out on screen and print it for submission. Form C-101 has been included so as to present the capabilities of the program. In the second case, a user can access the form written in hypertext as opposed to a word processing document directly from Netscape. Form C-103 shows an example of a hypertext form (**Figure 3** - Note: A hypertext form was not meant to be printed so the reader may see some discrepancies in the printed form which are not seen on screen.). This type of form can also be filled out on the screen and then transmitted to the OCD via email. This type of electronic filing hopefully will become standard in the future. The user can also click on the highlighted OCD rule which will provide the rule in its entirety. At the bottom of the procedures, the user has the option to click and see all the rules and regulations regarding drilling.

The second option on the Drilling Operations Menu is the EPA Classification of Wastes. This is a list of all the oil and natural gas exploration materials and wastes which are exempted by the EPA from consideration as "hazardous waste".

Production Operations. By selecting this menu option the program user is presented with five choices:

1.WQCC Definitions
2.EPA Waste Classification for Oil and Gas Exploration and Production Wastes
3.Ground Water Discharge Plans
4.Pits
5.Underground Injection Control

The first choice provides the WQCC (Water Quality Control Commission) definitions of environmental terms used in the WQCC regulations. The EPA Waste Classification is also presented again as a possible choice for the user. The third option is Ground Water Discharge Plans. This option instructs the user on how to prepare a ground water discharge plan for a natural gas processing plant, oil refinery or gas compressor station. Discharge plans are required by an operator of such facilities and indicate how the operator will comply with WQCC regulations in case of a ground water discharge.

The next possible selection is Pits. By clicking this link, the user will be presented another menu entitled Rules, Regulations and Guidelines for Pits. This menu offers three choices including:

1.Pit Orders

2.Pit Closure: Guidelines for Unlined Surface Impoundment Closure

3.Produced Water: Guidelines for the Selection and Installation of Below-Grade Produced Water Tanks.

Orders issued by the Oil Conservation Commission (OCC) address specific concerns, in this case pits, and only apply to the areas of the state specified within the order. Oil Conservation Division rules and regulations, on the other hand, apply statewide. The Pit Orders menu provides links which contain specific OCC orders which address environmental concerns related to OCD regulated facilities. The Pit Closure option provides recommended guidelines to close an unlined surface pit and the Produced Water option gives recommended guidelines for installation of below grade produced water tanks.

The last option presented in the Production Operations Menu is Underground Injection Control. By clicking on this option the user is given another menu: Rules, Regulations, and Guidelines for Underground Injection. From this menu there are two selections: 1) An overview of Underground Injection Control and 2) Injection Permitting. The first option gives an overview of underground injection control in the state of New Mexico. The second option shows permitting procedures for four different type of injection operations including:

- Pressure Maintenance Projects
- Water Flood Projects
- Salt Water Disposal Wells
- Storage Wells.

These permitting procedures follow the same framework as shown in the Permitting to Drill menu.

Pipeline Operations. This link has only one available option which is Guidelines for Hydrostatic Test Dewatering. This section is used as a guide for the preparation of plans and specifications for the discharge of water used in hydrostatic testing of new or existing pipelines that have or will transport hydrocarbons. Hydrostatic testing of these pipelines could lead to the production of contaminated water, which if not disposed of properly could be environmentally hazardous.

Abandonment Operations. By selecting this option, the user will see permitting procedures for three types of plugging and abandonment operations. Such operations include temporary, permanent and wells to be used for fresh water. The same framework for permitting is also continued in this menu section.

Leaks, Spills And Releases. The final menu choice is Leaks, Spills, and Releases. The user is then presented with Guidelines for Remediation of Leaks, Spills and Releases. This section instructs the user on what an operator should do in case of a leak, spill or release of an oilfield waste or product. The selection includes a step by step notification process that is required and also recommended remediation techniques.

State Of New Mexico Resource Directory. The last group of menu options includes resources outside of the OCD. The first choice provides another menu to resources just in the state of New Mexico. These resources are divided into five categories as follows: State Government Offices, Universities, Petroleum Industrial Organizations, Tribes and Pueblos and National Laboratories. The entire menu can be seen in **Figure 4**.

Environmental Resources On The Internet. By selecting this menu option the user is presented with two groups of hypertext links seen in **Figure 5**. One group is for federal government links and the second is for World Wide Web sites. The government group is divided up by departments of the government such as the EPA, Department of Energy and Department of the Interior. A link to the United States Code of Federal Regulations is also included. Through this particular link, a user can search all the federal rules and regulations of the U.S. government. Other World Wide Web Sites provides an extensive compilation of environmental resources around the world

New Mexico Oil Conservation Division Rules & Regulations. The last menu selection is the OCD rules and regulations. These are the general operating rules, not just environmental legislation but all rules, for the petroleum industry in the state of New Mexico. The rules are indexed and the user can easily move around in the hypertext format.

DISCUSSION

The hypertext environmental regulations manager is a beneficial tool for the engineer. In many exploration and production companies the engineers are responsible for environmental compliance and permitting work. By understanding the environmental operating guidelines initially, the engineer can work more responsibly with respect to the environment. This is becoming more and more important as stricter environmental regulations are being passed and implemented. In the state of New Mexico, OCD orders are also issued. These orders are rules that apply to specific areas of the state. For example, the northwest corner of the state is an environmentally sensitive area and lined pits are required for all well work in that area. Without knowing these orders, an engineer may inadvertently rig up on a well without using a pit liner. The

engineer's company could face large fines due to the engineer's lack of awareness of these statutes. By using the manager, it is possible that environmental violations could be avoided.

Engineers can spend several hours a day filling out regulatory forms. By using the regulations manager, the engineer can facilitate this process. For example, an engineer may spend three hours a day at $22 per hour ($45,760 per year salary) filling out such forms. Then, a secretary may spend another hour at $9 per hour ($18,720 per year salary) typing the forms. A company could easily spend $75 a day per engineer just on permitting requirements. This example is based upon the author's personal work experience with regulatory forms. Therefore, a large company with numerous engineers could spend a small fortune on permitting obligations. The number of days an engineer spends on permitting can vary, but if the engineer is working in an environmentally sensitive area, this number can only increase. With the regulations manager, the engineer can fill out the forms on screen and then print the forms which then only need the engineer's signature before they are sent off to the regulatory agency. By using the regulations manager, it is estimated that the time for the permitting process would be significantly reduced. If state regulatory agencies eventually convert to electronic filing, this process will be even faster.

The environmental regulations manager also provides a unique interactive method for conveying the environmental guidelines. People respond better to this type of training rather than studying manuals as shown by Rudolf Novotny in his SPE paper "PC-Based Interactive Technical Training."[6] It is much easier to find an answer by pointing and clicking within a software program than flipping through possibly thousands of pages of reference materials. Even if the engineer has a unique problem outside the scope of the environmental guidelines of the manager, the engineer can still access a multitude of resources on the Internet to find an answer.

SUMMARY

The objective of this study was to develop a method to assist the petroleum engineer in the environmental regulations aspect of the petroleum industry in the state of New Mexico. The hypertext environmental regulations manager accomplishes this objective in an interactive and intuitive manner. The main focus of this research was the recommended environmental guidelines of the New Mexico Oil Conservation Division.

The regulations manager, written in HTML, organizes and presents the recommended guidelines in five categories most useful to the production or reservoir engineer. These categories include drilling, production, pipeline, abandonment operations, and leaks, spill and release response. The manager also provides permitting requirements and procedures for environmentally sensitive operations such as drilling, injection and abandonment work. Along with the permitting procedures, OCD operating rules are presented which correspond to each specific procedure. The permitting procedures section

includes the necessary forms to be filed for each work procedure. Two types of on-line forms, a word processing format and a hypertext format, were shown. Using the hypertext format, the regulations manager connects the engineer to the rest of the environmental world with Internet hyperlinks to invaluable resource information. These resources included such World Wide Web sites as the Environmental Protection Agency and other U.S. federal government departments along with commercial environmental sites.

CONCLUSIONS

1.The hypertext environmental regulations manager is a unique tool that provides the New Mexico OCD recommended environmental guidelines, the permitting procedures required for environmentally sensitive oil and gas operations, and Internet links to environmental resources.

2.The environmental regulations manager can be a beneficial time-saver for the engineer when it comes to the required governmental permitting processes.

3.The environmental regulations manager introduces a new way of filling out regulatory forms on screen and a new method of filing the forms electronically. Electronic filing may be the standard in the future.

4.Engineers are more responsive to an interactive point and click software program as opposed to searching through volumes of rules and regulations.

5.The environmental regulations manager provides a unique method for instruction on the environmental side of the petroleum industry which in turn can help the engineer work more responsibly with respect to the environment.

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REFERENCES

1. Blaylock, R.E., Martin, F.D., Emery, R.: "Implementation of a World Wide Web Server for the Oil and Gas Industry," SPE 30214, presented at the 1995 SPE Petroleum Computer Conference, Houston, Texas, 11-14 June.

2. Zeltser, Lenny: "The World Wide Web, Origins and Beyond," World Wide Web Universal Resource Locator: http://homepage.seas.upenn/~lzeltser/ WWW/.

3. Lo, C.F.: "Development of an Intelligent Hypertext Manual for the Space Shuttle Hazardous Gas Detection System," NASA-CR-191898, Semi-Annual Report, University of Tennessee Space Institute, 1 July - 31 December 1992.

4. Cerf, Vincent: "How the Internet Came to Be, Part 1," World Wide Web Universal Resource Locator: http://sage.cc.purdue.edu/~xniu/winsock.htm.

5. Hughes, Kevin: "Entering the World-Wide Web: A Guide to Cyberspace," World Wide Web Universal Resource Locator: http://www.hcc.hawaii.edu /guide/ www.guide.html.

6. Novotny, Rudolf, J.: "PC-Based Interactive Technical Training," SPE 30189, presented at the 1995 SPE Petroleum Computer Conference, Houston, TX, 11-14 June.

NEW MEXICO

Environmental Regulations Manager

Welcome to the New Mexico Environmental Regulations Manager. This hypertext document will allow the petroleum engineer to quickly locate environmental guidelines pertaining to their area of work and gives an overview of exploration and production operations environmental regulations as governed by the New Mexico Oil Conservation Division.

New Mexico Oil Conservation Division (OCD)

- Overview of OCD Environmental Regulatory Programs
- OCD Function Chart
- OCD Personnel Organization Chart
- Delegation of Authority for Oilfield Exploration & Production Operations
- Water Quality Control Commission
- OCD Telephone Directory
- Map of OCD District Offices

For Rules, Regulations & Guidelines by Subject, Please Select Your Area of Interest.

- Drilling Operations
- Production Operations
- Pipeline Operations
- Abandonment Operations
- Leaks, Spills or Releases

State of New Mexico Resource Directory

Environmental Resources on the Internet

New Mexico Oil Conservation Division Rules & Regulations

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Figure 1-The Homepage of the Environmental Regulations Manager

Permitting for a Single Completion Well

The following must be completed prior to spudding well:

1. A plugging bond must be filed in the Santa Fe office of the OCD for approval as per RULE 101. Bonds may be in the form of One-Well or Blanket.
2. Five copies of Form C-101: **Application for Permit to Drill** must be filed with the appropriate OCD district office as per RULE 1101.
3. Three copies of Form C-102: **Well Location and Acreage Dedication Plat** must also accompany Form C-101 as per RULE 1102. Acreage requirements must be met as per RULE 104.
4. If well is to be drilled on U.S. Government Land, then the Application for Permit to Drill must be filed on Bureau of Land Management Form No. 3160-3.
5. A blowout prevention program must also be submitted with Form C-101 as per RULE 109.

The following must be completed upon commencement of drilling operations:

1. Form C-103: **Sundry Notices and Reports on Wells** must be filed in triplicate within 10 days of commencement of drilling operations to indicate hour and date the well was spudded as per RULE 1103.
2. Form C-103 must be filed in triplicate to report casing and cement job test results.

The following must be completed upon termination of drilling operations:

1. Five copies of Form C-105: **Well Completion or Recompletion Report and Log** must be filed within 20 days of termination of drilling operations as per RULE 1105 along with a summary of all tests performed on well.

OCD Rules Regarding Drilling

Return to Drilling Operations Menu

Figure 2.- Permitting Procedures for a Single Well Completion

State of New Mexico

Energy, Minerals and Natural Resources Department

OIL CONSERVATION DIVISION

P.O. Box 2088

Santa Fe, New Mexico 87504-2088

C-103: Sundry Notices and Reports on Wells

Please note: Although it is most unlikely that you will experience any problems responding to this form, certain non-standard browsers will not respond properly. If you experience any difficulties, (or if you are not using a forms-capable browser) you may email your response to this form to: forms@ocd.gov.

Type of Well: Oil Well Gas Well Other

Name of Operator:

Address of Operator:

Well API Number:

Indicate Type of Lease: State Fee

State Oil and Gas Lease Number:

Lease Name or Unit Agreement Name:

Well Number:

Pool name or Wildcat:

Well Location: Unit Letter:

Feet from the Line and Feet from the Line.

Section: Township: Range:

NMPM: County:

Elevation:

Check Appropriate Box to Indicate Nature of Notice, Report, or Other Data.

NOTICE OF INTENTION TO:
Perform Remedial Work
Temporarily Abandon
Pull or Alter Casing
Plug and Abandon
Change Plans

Other

Other Intention:

SUBSEQUENT REPORT OF:
Remedial Work
Commence Drilling Operations
Casing Test and Cement Job
Altering Casing
Plug and Abandonment
Other

Other:

Describe Proposed or Completed Operations: (Clearly state all pertinent details, and give pertinent dates, including estimated date of starting any proposed work.) SEE RULE 1103.

I hereby certify that all the information above is true and complete to the best of my knowledge and belief.

Name:

Title:

Date:

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Figure 3- Hypertext Form C-103: Sundry Notices and Reports on Wells

State of New Mexico Resource Directory

New Mexico State Government Offices

New Mexico Office of the Bureau of Land Management (BLM)
New Mexico Environment Department (NMED)
New Mexico State Land Office (SLO)
Other New Mexico State Offices (Other)

New Mexico Universities

New Mexico Institute of Mining and Technology (NM Tech)
New Mexico Petroleum Recovery Research Center (PRRC)
New Mexico Bureau of Mines and Mineral Resources (NMBMMR)
Petroleum and Natural Gas Engineering Department (Pet. Dept)
Geosciences Department (NMT)
New Mexico State University (NMSU)
University of New Mexico (UNM)

New Mexico Petroleum Industrial Organizations

Independent Petroleum Association of New Mexico (IPANM)
New Mexico Oil and Gas Association (NMOGA)

Native American Tribes & Pueblos Environmental Index

National Labs in New Mexico

Los Alamos National Laboratory (LANL)
Environmental Systems (ES)
Sandia National Laboratory (SANDIA)
Energy & Environment Sector (EES)

Figure 4-State of New Mexico Resource Directory

ENVIRONMENTAL RESOURCES ON THE INTERNET

Federal Government Links

Environmental Protection Agency (EPA)
EPA Region 6
The National Evironmental Policy Act (Act)
Department of Energy (DOE)
Energy Information Administration (EIA)
Office of Fossil Energy (OFE)
Department of the Interior (DOI)
Bureau of Indian Affairs (BIA)
Bureau of Indian Affairs Division of Energy & Mineral Resources (BIA-DEMR)
Bureau of Land Management (BLM)
Bureau of Mines (BOM)
Minerals Management Service (MMS)
United States Geological Survey (USGS)
U S. House of Representatives Internet Law Library - Code of Federal Regulations (CFR)
Chapter 40 - Oil Pollution (Ch. 40)
Chapter 103 - Comprehensive Environmental Response, Compensation & Liability (Ch_103)

Other World Wide Web Sites

Bioremediation (Bio)
Environmental Professional's Homepage (EPH)
Environmental Resources on the 'Net (ERN)
Groundwater Remediation Technologies Online Resource Guide (GRT)
Internet Environmental Resources (IER)
Texas Environmental Library & Resource Center (TELRC)

Return to Main Menu

Figure 5 -Environmental Resources on the Internet

Coming to Grips with Environmental Management and Auditing Systems; Today's Challenges for Non-Majors

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Abstract:

Environmental management programs have become an integral part of good management practice for many large companies involved in the oil and gas industry. Despite the fact that a strong environmental management program produces sufficient benefits to justify its existence, most small companies have not adopted such programs as part of their management philosophy. Small companies may realize that environmental violations of a repetitive nature and conduct which could lead to criminal prosecution could be virtually eliminated by such programs, but feel they lack the personnel, management skills and budget to be able to realize these benefits. Small companies feel they cannot justify spending precious resources in pursuit of abstract goals such as using auditing to decrease the chance for the kind of incident which harms the environment and tarnishes the industry's relations with regulatory agencies and the public. On the negative side, small companies do understand that auditing could pose a significant new risk of increased exposure to civil and criminal liability and feel more vulnerable to such threats because one large lawsuit could wipe them out. Despite these hurdles, more and more small oil and gas companies are considering the use of environmental management programs including auditing. This paper reviews the way a small operator should go about determining whether or not to adopt such a program and describes legislative and regulatory developments which could minimize the legal impediments to a small company entering the environmental auditing age.

HISTORICAL PERSPECTIVE

The environmental audit is not a new concept. During the twenty-five years since the United States passed the first wave of major environmental legislation, methods for assessing the degree to which a company's operations conform to the requirements of those laws have evolved. Some regulatory agencies have recognized that self-auditing should be a significant tool in achieving regulatory compliance. Outside the environmental area, the FAA has had significant success through the use of self-inspection by air carriers.[1] The Federal EPA has been working on this issue for more than a decade[2] and published a policy designed to encourage environmental auditing by regulated entities in 1986[3]. The EPA has been unable to generate any significant increase in auditing activity because the agency views itself, primarily, as a law enforcement agency. The EPA and the Justice Department both use statistics on the amount of fines levied and the number of criminals put behind bars as evidence of the success of their enforcement programs, when, in fact, they are indices of the failure of their present punishment oriented system.

The major barrier to the broader use of the auditing process has been the threat that the results of voluntary audits would be used by government agencies, plaintiff's lawyers and environmental groups against the people and company doing the audits[4]. Most corporate auditing programs are conducted under a policy which requires heavy legal department involvement. How the audit is done and who is allowed to take part is dictated by defensive legal considerations. Communication of audit results is restricted to those whose involvement will not destroy the attorney-client privilege or the attorney work product privilege. This restrictive and controlled process and the legal/regulatory system which makes it necessary make it impossible for the company, its industry, the environment or society to fully benefit from the auditing work which is being done. A company may not be able to share environmental lessons learned or safety information discovered in the audit of one facility with those at its other facilities. Company representatives cannot share audit results with their peers in Industry or professional groups and government agencies cannot fully interact with industry in dealing with potential environmental risks or safety hazards.

In addition, citizens' suit provisions, which are found in almost every one of our nation's environmental laws, provide plaintiff's lawyers and environmental advocacy industry groups with a tool for demanding access to a company's audit reports. Under these provisions, private citizens can and do sue to block or overturn agency actions, such as granting a permit, and also to seek damages and to force compliance with what these groups perceive as being the regulatory requirements.

Since the lead federal environmental agencies use convictions and fines to justify their programs and nothing they do can control third party lawsuits, agency auditing policies can never be the most effective way to promote the adoption of new corporate environmental auditing programs. Even the existence of immunity provisions in the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)[5] and the Clean Water Act [6] are ignored by the agencies in their effort to portray the enactment of new federal audit legislation as radical and anti-environment. Only legislative action will be able to provide the clear and dependable guidelines necessary to bring about the widespread adoption of new environmental auditing programs.

STATE LEGISLATION

In an attempt to create a legal regime under which cooperation and mutual respect would replace the present punishment-oriented legal system eighteen states[7] have passed various new laws based on the self-critical analysis privilege. These laws are designed to create a new social contract which will stimulate more audit activity. Under the new state laws, companies expend time, effort and monetary resources to do a large portion the job of assuring that the state's environmental laws are being complied with and must remediate problems arising from violations discovered during the process in a timely fashion. In return, in specific situations set forth in the new laws, the state gives up the power to fine the companies and keeps the contents of the environmental audit confidential. In addition, the auditors themselves are kept free from being forced to testify regarding what they learned and did during the audit.

State audit legislation is still evolving. The ground-breaking Oregon statute creates a limited evidentiary privilege while later laws create both limited privileges and limited immunity from civil penalties, and in some cases, from the prosecution for some acts which are defined as "criminal" in some statutes despite the fact that no criminal intent is required. In some states the laws extend the applicability of the limited evidentiary privilege and immunity to actions filed on behalf of non-governmental entities or brought under "citizen suit" provisions in many federal laws. There are significant differences in content between the state laws, but the following outline illustrates how a generic privilege and immunity statute is supposed to function:

1. The regulated company would set up an auditing program, usually as part of a broader environmental, safety and health management program;

2. The company would conduct environmental audits, as defined in their state' law, on a routine basis;

3. If the results of one of these routine audits include the discovery of a likely violation of an environmental law, the company could reveal this fact to the appropriate state agency, end the violation and promptly begin action needed to remediate any effects of the violation;

4. If the remediation is likely to take longer than the base period allowed under the law, the company would consult with the state agency to work out an appropriate schedule for the completion of the work; and

5. If a governmental agency feels that a company is not entitled to assert the privilege and/or claim immunity, the agency may take the matter before a judge in an *in camera* hearing to obtain a determination of the company's claims.

Adopted in states like Texas, Colorado, Michigan and Minnesota on a bi-partisan basis[8] and sometimes even with the support of their attorney general, local environmental groups, the state environmental agencies and local prosecuting attorneys, this win-win concept has run into a firestorm of opposition from national environmental groups[9], the National District Attorneys Association[10], and the Clinton Administration's EPA and Justice Departments[11]. These Federal Agencies have opposed federal audit legislation[12] and carried out an aggressive, unprecedented, anti-legislation lobbying campaign in state legislatures where audit bills are being considered[13]. The EPA has even formed a task force[14] which seems to be trying to force states which have adopted laws to change them or issue regulations which modify them to EPA's liking by withholding any pending EPA approvals of delegated programs[15]! Supporters of the legislation have been attacked by the Vice-President and EPA and Justice officials. They have been characterized as evil plotters who are trying to prevent environmental criminals from being prosecuted and who are trying to gut the nation's environmental laws in order to make profits from the destruction of the environment! States which have passed laws have been threatened with losing the ability to administer federally mandated environmental regulations like Title V of the Clean Air Act. Although it is unclear how the EPA could find the personnel or funds to administer all these laws if it took them away from the states, this campaign of intimidation is being waged with increasing intensity as more and more states adopt or consider the enactment of new laws. Ironically, it is compliance with laws like the Clean Air Act with complicated sets of regulations that would benefit the most from the implementation of state audit laws.

EPA AUDIT POLICY

Since eighteen states have adopted legislation designed to promote

new auditing and environmental management programs and legislation has been introduced in both the Houses of Congress, the EPA has responded by issuing a new policy on environmental auditing[16] which they hoped would take away the need for further legislation. This new policy evolved through several interim documents over the past five years, contemporaneously with the emergence of state legislation as a major issue.

The EPA policy recognizes that maximum compliance with environmental regulations can only be achieved if limited government resources are augmented by a substantial, self-policing effort on the part of regulated industries. The EPA promises to waive gravity-based civil penalties except for any economic gain from noncompliance to companies which exercise "due diligence" through the adoption and implementation of a systematic compliance management system to audit their operations and whose actions meet the following conditions:

1. discovery of the violation was totally voluntary;

2. disclosure to the EPA is made within ten days of the discovery of the violation or potential violation or any shorter period required by law;

3. discovery and disclosure are made independently of any action on the part of any government agency or third party plaintiff;

4. action to correct and remediate is taken promptly;

5. action is taken to prevent recurrence of the violation;

6. the company has no history of repeat violations;

7. the violation did not result in serious actual harm or present an imminent and substantial endangerment to human health or the environment, or violate the terms of any judicial or administrative order or consent agreement; and

8. the company cooperates fully in the investigation of the violation and all related matters.

This restrictive set of conditions and other limitations of the EPA policy have prevented it from meeting with acceptance in the regulated community. AS a mere "policy" the promises made are not even binding on EPA Regions, which have a reputation for taking independent courses of action from time to time. Certainly it has no power to bind other federal, state or local agencies or third parties. By making public the information supplied by

companies seeking shelter under the policy, the EPA provides plaintiff's attorneys and enforcement agencies with a veritable invitation to sue. In fact, the EPA itself could use the information supplied to begin its own investigation of other company facilities or activities. The company trying to satisfy the policy's conditions could find that the EPA would get access to otherwise privileged documents. The requirement that the company not have a "history of repeat offenses" could mean that most companies would never qualify because violations tend to be of the same type despite a company making the best efforts to prevent them. The condition requiring prompt disclosure also covers "potential violations"...ones which "may have occurred"... and these potential violations would be made public! There would be no consistency or certainty of outcome because the decision on whether the conditions have been met is based on so many subjective judgments by so many people. Finally, since violations which may present an imminent and substantial endangerment to human health and the environment do not qualify for protection under the policy, most violations in the oil and gas industry would not qualify because courts have interpreted that terminology to include almost any release of chemicals, even where there is no actual harm demonstrated[17].

Although this national policy is the EPA's official position, Region I in Boston has launched its own program called "Startrack". It is an ambitious attempt to "expand the use of environmental compliance and management system audits to improve environmental quality, public understanding of a company's environmental performance and [redeployment of taxpayer resources.[18]" Meetings of stakeholders began on August 28, 1996, in an attempt to work out the details of how such a program would function. Ten companies which operate in Region I have volunteered to be part of a pilot, first phase which will attempt to see if this program holds any promise. The main stumbling blocks to its gaining wide acceptance are its reliance on third party audits and the public disclosure of all audit findings.[19] More will be written about this experimental program as it progresses.

ENVIRONMENTAL AUDIT PROGRAMS

Now that we have made a quick review of the regulatory and legislative environment in which auditing programs must be carried on, lets take a look at the process which could be utilized by smaller oil and gas operators in considering the pros and cons of adopting a new environmental management and auditing program.

The environmental audit process was first defined and carried out by large corporations in the energy, power and chemical industries. As a critical part of an overall environmental management system, it is still evolving in its content, format and scope even as its role in good overall business

management is becoming more and more apparent. Anyone who has looked into the environmental audit process has found it to be complex and dynamic. Possible legal entanglements detailed above, a fundamental review of management's role in controlling environmentally critical operations, and the need to commit increasing amounts of corporate resources in both time and money are of concern to those with existing auditing programs and to those who are thinking of starting one.

Major oil and gas corporations have environmental management programs with auditing components and have blazed the trail for smaller companies to follow. Experience gained and changes in laws and regulations are now being factored in as existing programs or the adoption of a new program is reviewed in-house, and in connection with the offshore industry's work with the Minerals Management Service on the voluntary implementation of API RP 75[20] and in the development of ISO 14000 series standards[21]. Groups such as ANSI[22] and the Environmental Auditing Roundtable[23] have also adopted standards of use in designing and implementing new programs.

With the maturation of the field of environmental auditing and the availability of increasing numbers of qualified audit consultants, generic auditing programs and professional group standards to use as references, smaller corporations can begin to plot their own course. One clear lesson from past experience is that in establishing or reviewing an environmental management and auditing program, careful collection of facts and full consideration of the nature and scope of alternative courses of action will save much trouble an money later on. Another lesson is that environmental audits should not be carried out until after a company has considered and understood all the implications of auditing and has established a formal corporate environmental management program.

PRE-PROGRAM OR PROGRAM REVIEW PROCESS

Since one of the tenets of an environmental management and auditing program is that all of its goals and procedures must be periodically reviewed, the following process should be revisited every five years or so. Each year a corporate environmental compliance profile should be compiled. This profile will give an annual check on whether the program's goals are being met and could indicate if there is the need for an immediate, overall program review.

The pre-program review provides a company with the information it needs in order to decide whether or not to establish an environmental management and auditing program. It should be carried out by a high level

management team including legal, operations and policy level members. Any existing corporate environmental policy, environmental action program or environmental compliance activities should be examined. Next, an up-to-date list of corporate activities which have environmental implications should be complied. Each identified activity should be listed along with citations to the law and regulations which set the limits for corporate activity. Also identified should be the possible penalties for the violation of each regulation and the job title(s) of the person(s) responsible for corporate compliance.

Based on this information, the scope of a possible environmental audit program should be delineated. Overall environmental management program goals, methods, manpower requirements, any new equipment needed, a start-up cost estimate and a target date for completion of a final report should be set. Once a program is agreed on in draft form, the task force should stop and discuss any possible alternative programs or policies which could achieved the same overall company goals. Any promising alternative should be reviewed and evaluated on legal, economic and technical grounds before the task force decides on its final recommendation. Any serious alternatives which were considered should be described in the final report along with the reasons why they were rejected. This will be very helpful during future program reviews. If the task force's final report calls for the establishment of an environmental management and auditing program, a detailed timeline for program implementation should be set forth.

The experience and education gained during this pre-program review by key members of management and legal staff will serve as a sound basis for the actual implementation and operation of the environmental management and auditing program. The same group which was assembled to
decide on the adoption of a program should follow the same sort of process in conducting periodic reviews of the program the company adopts.

RISK OF PROSECUTION

The risks faced as the result of discoveries during an environmental audit are civil suits, administrative penalties and/or criminal prosecution of the company and/or its individual employees. Therefore, it is easy to understand why the need to consult with legal counsel in setting up and running an auditing program cannot be overstressed.

It is inevitable in a complex business such as the offshore oil and gas industry that even the most effective company policy for achieving compliance with environmental laws will not prevent the occasional discovery of a violation of some regulation. The knowledge that a violation has taken

or is taking place in turn creates a duty to communicate that information to the appropriate government agency or risk civil and even criminal prosecution. If the state in which you are operating has adopted legislation which grants a privilege to audit reports and immunity from agency civil penalty actions, this duty to disclose your knowledge to the state may be considerably less threatening.

Recently Congress has amended the penalty provisions of a number of environmental laws and has also passed the Pollution Prosecution Act of 1990. Criminal penalties have been added by Congress and state legislatures and the Pollution Prosecution Act required the EPA Administrator to triple the number of criminal investigators in EPA's Office of Criminal investigations by October 1, 1995. This illustrates the political pressures on the EPA and Justice Department to prove that they are tough on environmental violators. In this sort of atmosphere, those agencies are unlikely to do anything which would be interpreted as being "soft" on apparent violations of environmental laws. This political pressure is likely one of the major reasons why these agencies have opposed state audit encouragement legislation.

What should management do if information collected during the routine environmental audit reveals a potential criminal violation? The laws require prompt reporting of violations to the appropriate agency. Failure to report can make a civil violation into a criminal case. Even if the audit was designed to be covered under the attorney-client privilege, there may be a duty on individual auditors or on management to report a violation uncovered by the audit. If the audit material would show that the company gained knowledge of a spill but failed to report it, could criminal charges be brought against the company, its field employees and its top management?

Scenarios should be developed and clear guidance devised by legal counsel during the development of an Environmental Management and Auditing Program so that all managers and workers understand what they are required to do in such questionable situations.

Actually, this sort of risk of prosecution is not solely produced by environmental audits. It is inherent in any system which creates a very detailed, written record of the conduct of the company and its employees with regard to regulatory compliance. Even if a company does not carry out environmental audits, there are many discoverable records which are kept as part of its routine business operations or as a result of environmental and non-environmental regulations. These records could be used by a regulatory agency during an investigation or by a third party in a private lawsuit. Daily drilling reports, mud company reports and other forms in common use contain business information and also some material required by law. Although

questions which an agency investigator would be interested in, other records can be pieced together to tell the same story to the investigator.

In the end, each company must balance the benefits expected from a well run Environmental Management and Auditing program and the possible increase in risk from keeping additional records. These programs require free and complete management access to all information relevant to achievement of environmental compliance goals before they can improve a company's environmental compliance while also increasing its efficiency and profitability. States which have passed audit legislation have tried to create a climate where this win-win objective can be achieved. The adoption of federal legislation similar to bills adopted in Michigan, Texas and Colorado, is the only way the conflict between the federal enforcement agencies' policies and state legislation can be eliminated

CONCLUSION

Given the rapid proliferation of environmental laws world-wide, Environmental Management and Auditing programs should now be considered to be an integral part of the management structure all oil and gas companies. Non-majors must find innovative ways to use outside expertise and information within their manpower and budget constraints so that they can realize the benefits that flow from greater control over their operations.

The effectiveness of an Environmental Management and Auditing Programs can only be maximized when governments' legislative bodies and regulatory agencies assume a more positive role in encouraging and aiding the development of such programs. The Minerals Management Service has done its part by working with the American Petroleum Institute and its offshore members in developing the SEMP program based on API RPs 75 and 14J. The EPA and the Justice Department have to do their part by eliminating their alarmist, anti-audit rhetoric against the states and become helpful but vigilant observers of the functioning of the states as Justice Brandeis' "laboratories of federalism, where legislative innovation may be tried for the potential benefit of the entire nation"[24]. Results so far under the Texas audit legislation indicate that, given the chance, companies are acting in good faith, auditing more and coming forward to take responsible actions under that state's guidelines. If they are acting in good faith, the EPA and Justice Department should be able to justify assuming a more positive role where industry conduct demonstrates that a cooperative policy will result in the achievement of the states' legislative goal of improved environmental compliance. The passage of federal audit encouragement legislation should take place, but only after the experience gained under the various state laws has been studied and factored into the drafting of the federal statute.

CITATIONS

1. FAA Advisory Circular 120-56, "Air Carrier Voluntary Disclosure_ Reporting Procedures", January 23, 1992, and FAA Advisory Circular 120-59, "Air Carrier Internal Evaluation Programs", October 26, 1992.

2. Weiss, Malcolm, "Issues of Confidentiality and Disclosure in Environmental Auditing", Report No. EPA-230-11-85-015, April, 1984.

3. U.S.EPA,"Environmental Auditing Policy Statement", 51 Fed. Reg. 25004, July, 1986.

4. Price Waterhouse LLP, "The Voluntary Environmental Audit Survey of U.S. Business", March, 1995.

5. 42 U.S.C. Section 9601 *et seq.* (1993).

6. 33 U.S.C. Section 1321(b)(5) (1993).

7. See Handout, "Analysis of State Audit Legislation", Perkins Coie, Washington, D.C., March, 1996, Contact Jim Moore, Esq. (206) 583-8898 or Nancy Newkirk, Esq., (202) 434-1610.

8. "Minnesota Environmental Improvement Pilot Program', May, 1995, passed - House, 128 to 1 - Senate 64 to 0.

9. Testimony of Mark Woodall, The Sierra Club, re: S.582, before U.S. Senate Committee on the Judiciary, Subcommittee on Administrative Oversight and the Courts, May 21, 1996, and Christopher Bedford, "Dirty Secrets, The Corporations' Campaign to Create an Environmental Audit Privilege", Communities Concerned About Corporations, the Environmental Action Foundation and the Good Neighbor Project for Sustainable Industries, (1996).

10. Testimony of Hon. Victor S. Johnson, District Attorney General, 20th Judicial District, Nashville, TN., before the U.S. Senate Committee on the Judiciary, Subcommittee on Administrative Oversight and the Courts, May 21, 1996.

11. Testimony of Steven A. Herman , Assistant Administrator, OECA, and a Joint Statement of Veronica Coleman, United States Attorney, Western District of Tennessee and Lois Shiffer, Assistant Attorney General, Environment and Natural Resources Division, to the United States Senate, Committee on the Judiciary, Subcommittee on Administrative Oversight and the Courts, May 21, 1996.

12. Letter dated December 6, 1995, from Sheldon N. Light, Assistant U.S. Attorney, Eastern District of Michigan to Ms. Teri Quimby, Michigan House of Representatives, and Memorandum dated February 12, 1996, from Mr.Lynn Helland, Supervisory Assistant U.S. Attorney, Eastern District of Michigan, to the Michigan House of Representatives, Committee on Conservation, Environment and Great Lakes.

13. Memorandum dated March 18, 1996, from Steven A. Herman, Esq. Assistant Administrator, U.S. EPA, to various EPA officials including all Regional Administrators and another Memorandum dated April 5, 1996, from Steven A. Herman, Esq.,

Assistant Administrator, OECA, and Mary Nichols, Assistant Administrator, OAR, to Jackson Fox, Esq., Regional Counsel, Region X.

14. RE: Idaho and Other States' CAA Title V Operating Permits, Statement of Bob Jackson, EPA Region X Spokesman, March 25, 1996, and Editorial, "An Agency with an Attitude", *Rocky Mountain News*, August 26, 1994.

15. U.S. EPA, Final Policy on "Incentives for Self-Policing; Discovery, Disclosure, Correction and Prevention of Violations", 60 **Fed.Reg.** 66706-66712, December 22, 1995.

16. **U.S.** v. **Conservation Chemical Company**, 619 F. Supp. 162 (W.D. MO. 1985).

17. U.S. EPA Region I, Undated Press Release and "3PC" Application Form, EPA Contact - George Hawkins at (617) 565-9125.

18. Jean H. McCreary, Esq., President, The Environmental Auditing Roundtable, Comment Letter dated May 1,1996, to Gina Snyder, Coordinator, Environmental Leadership Program, EPA Region I.

19. American Petroleum Institute, RP 75, "Recommended Practices for Development of a Safety and Environmental Management Program for Outer Continental Shelf (OCS) Operations and Facilities", May 15, 1993.

20. International Standards Organization Technical Committee on Environmental Assessment 14,000 Series Environmental Management Systems Standards, ISO 14,001 " Specifications with Guidance for Use"; ISO 14,004 "General Guidelines on Principles,Systems, and Supproting Techniques"; 14,010 "Environmental Auditing - General Principles"; 14,011 "Environmental Audit Procedures - Auditing Environmental Management Systems"; and 14,012 "Qualification Criteria for Environmental Auditors".

21. American National Standards Institute, Standards Catalog, on the Internet at <http://www.ansi.org>.

22. Environmental Auditing Roundtable, Standard for the Design and Implementation of an Environmental, Health, and Safety Audit Program, Copyright, 1995.

23. **New State Ice Company** *v.* **Liebmann**, 285 U.S. 262 (1932), Dissent by Justice Louis D. Brandeis.

Compliance With Statutes and Regulations: No Safe Harbor Against Liability for Common-Law Negligence

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ABSTRACT

In the petroleum industry, environment, health and safety management is responsible for developing and implementing programs and procedures to insure that line management and operational personnel comply with environmental and safety laws and regulations enacted at the federal, state and local level. To be effective, these programs must be implemented during the engineering and design stages, and continue through to the quality assurance phase. The industry knows that to operate successfully over the long term, it must function within the law. However, recently, as the competitive environment of business tightens, restructuring places ever increasing demands on available personnel and operational budgets to insure bottom-line profitability. In response to these demands, some sectors of the industry have taken a bare-bones approach to regulatory compliance. Indeed, the EH&S department of one major American corporation has internally published an official position that "We will move beyond compliance only to achieve business goals."

This approach to cost-saving is based, at least in part, upon a false premise - that mere compliance is enough. This view is dangerous for the industry since, for over 100 years, the common-law rule has been that mere compliance with statutes, regulations, and standards of the industry is not enough to insulate a company from liability for negligent conduct, particularly when the situation demands that additional steps be taken. The fact is, successful tort claims effectively establish standards for operation, safety, and the protection of the environment. The result is a system of dual regulation. One system established by legislative enactment and administrative rule making, the other created, quite unpredictably, by six and twelve member groups sitting in jury boxes around the country. To protect the bottom line, the industry must take into account these common-law standards of conduct in order to avoid the significant effects of awards of compensatory and punitive damages which can easily reach into the millions of dollars.

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I. PRIMER ON NEGLIGENCE

A. *THE STANDARD OF CARE*

Before understanding how to avoid liability for negligence, the reader must first have a basic understanding of the legal concept. The general concept of negligence is widely understood to describe those situations where an individual either entirely fails to do that which he is expected to do, or performs a duty below the level society expects. The common-law defines negligence as "conduct which falls below the standard established by law for the protection of others against unreasonable risk of harm."[1] The most troublesome aspect of determining how to avoid a claim for negligence is determining what standard of conduct applies to a particular situation.

Generally, the common-law demands one to exercise "due care."[2] That is to say, an individual must act as a reasonably prudent person under the same or similar circumstances to avoid being negligent.[3] One standard does not necessarily apply to every situation or to every actor. The law recognizes that differing standards should be applied to children and incompetents, as well as to those possessing special skills. For example, when dealing with especially hazardous instrumentalities such as electricity or propane,[4] the courts expect those involved to exercise "the highest degree of care."[5]

Before the jury can resolve the question of a defendant's negligence, the applicable standard of conduct must be determined by the court. The standard may be adopted from prior judicial decisions, statutes or regulations which provide specifically that the particular standard shall apply to civil negligence actions, or from those statutes and regulations that were not originally intended to be applicable to such lawsuits. In the absence of such sources of reference, the judge or jury may apply the particular facts of the case to arrive at an entirely new standard.[6] Once the required level of performance is determined, the question of whether a defendant complied with such standard of conduct, *i.e.*, whether the defendant exercised due care, is left for the jury to decide.[7]

B. *THE DOCTRINE OF NEGLIGENCE PER SE*

It is settled that a court can adopt the requirements of a statute or regulation to establish the standard of conduct required of a defendant under particular circumstances, even if the statute or regulation does not directly apply to claims for tort liability. Generally, a court will only adopt a standard of conduct from a statute or regulation if that statute or regulation was intended, at least in part, to protect the class of persons to which the plaintiff belongs from the specific type of harm which actually resulted from its violation.[8] Thus, a violation can have a direct bearing on a finding of negligence, and is generally used in one of two ways. In a few jurisdictions, the fact of the violation creates the inference that the defendant did not exercise due care, and is only one factor in determining

negligence.[9] However, the majority of jurisdictions hold such a violation to be negligence *per se*, thus, the fact of the violation conclusively establishes the defendant's negligence.[10]

Penal statutes and regulations are particularly likely to be adopted as providing a minimum standard of conduct. Although courts are not required to adopt these statutes and regulations as establishing the standard for civil liability,[11] many courts take the view that the reasonable person would obey the criminal law; therefore, one who violates the law must be negligent.[12] Once negligence has been shown, all that remains to establish the defendant's liability is proof of the plaintiff's injury and the causal connection between the injury and the violation.[13]

II. THE SYSTEM OF DUAL REGULATION

A. *THE PROBLEM OF REGULATION IMPOSED BY COMMON-LAW*

The fact that a violation of a statute or regulation may establish negligence does not necessarily lead to the conclusion that compliance demonstrates due care.[14] This is so since, in most circumstances, statutes and regulations are viewed as establishing only the bare minimum threshold of acceptable conduct.[15] Courts can, and often do, hold that the civil law imposes a standard of conduct which is higher than that described by statute or regulation.[16]

Thus, a lawyer attempting to use a defendant's compliance with the applicable statutes and regulations as an absolute defense to common-law tort liability is likely to fail. Section 288C of the RESTATEMENT (SECOND) OF TORTS has been cited nationwide[17] for this proposition, and provides:

> Compliance with a legislative enactment or an administrative regulation does not prevent a finding of negligence where a reasonable man would take additional precautions.[18]

It is apparent that the common-law standard of the "reasonable prudent man" can be applied by the courts despite a legislative enactment covering the same conduct or circumstances.[19] The result is that successful common-law tort actions have the effect of establishing standards which can be applicable to the same conduct prescribed by statute or regulation.[20]

Where does this leave the petroleum industry? In effect, the industry is faced with a system of dual regulation - one system imposed by legislative and administrative enactment, and the other imposed by courts and jurors. The industry simply cannot focus its environmental health and safety management efforts solely on attaining compliance with the applicable statutes and regulations, where a violation can mean fines, penalties, agency orders and injunctions.[21] It must also consider how its efforts compare to the standards of the industry and the state of technology, not only of today, but tomorrow as well. This is necessary to

anticipate where the judicial line defining the common-law standard of due care may be drawn, as a violation of that standard can mean the payment of compensatory and punitive damages, as well as orders from the court to cease operations and to remediate environmental conditions.[22] This can prove to be a difficult and speculative task, since juries are notoriously unpredictable, and such judicially determined standards of conduct are often vague, indeterminate,[23] and may vary from location to location, even within the same jurisdiction.

B. *THE HISTORY OF THE DOCTRINE*

There is nothing new about the industry's predicament. Industry has been faced with this parallel system of regulation since at least 1892 when the Supreme Court ruled in the landmark case of *Grand Trunk Railway Co. v. Ives*,[24] that compliance with statutes provided no defense in a suit for negligence.[25]

The railroads were one of the first industries in the country to be systematically regulated.[26] As lawsuits were brought against the railroads, primarily for deaths occurring at grade crossings, railroad companies responded by asserting their compliance with the requirements of the applicable statutes as an absolute defense.[27] In *Ives*, the Court settled the issue when it announced:

> It is also held in many of the states (in fact the rule is well-nigh, if not quite, universal) that a railroad company, under certain circumstances, will not be held free from negligence, even though it may have complied literally with the terms of a statute prescribing certain signals to be given, and other precautions to be taken by it, for the safety of the travelling public at crossings.[28]

The Court did not erase the compliance defense altogether. The Court implied that efforts in excess of those compelled by the statute may only be required in circumstances where extraordinary hazards exist.[29] Nonetheless, into the modern era, railroad companies consistently have been exposed to civil liability by application of the same rule established over 100 years prior.[30]

C. *SOME REPRESENTATIVE CASES*

Courts have not been reluctant to apply the rule of RESTATEMENT Section 288C to a broad spectrum of tort suits brought against regulated industries. For example, compliance with building codes has been held as no defense to actions for negligent design or construction.[31] Compliance with water craft operation regulations was held no defense to a wrongful death action when a diver was struck by a commercial whale-watching vessel.[32] Electrical utilities find little protection in their compliance with national and local electrical codes when sued for negligent placement of their power lines.[33] Propane suppliers who followed the requirements of odorization regulations found their compliance to be no insulation from liability for explosions due to undetected gas.[34] And, product manufacturers

discovered that compliance with federal and local statutes and regulations still leaves open the possibility of liability for negligent design.[35]

Of greatest interest to the petroleum industry are those cases involving highly-regulated industries, where even the direct approval of the defendant's activities by the responsible administrative agency is inadequate to provide a defense to tort liability. For example, aircraft designs must be approved by the Federal Aviation Administration, and aircraft manufacturers maintain that due to the complexity of their product, agency approval should be conclusive as to the reasonableness of their designs.[36] However, in *Cleveland v. Piper Aircraft Corp.*,[37] a personal injury action brought against an aircraft manufacturer for negligent design, the Tenth Circuit Court of Appeals held that the FAA's approval of the aircraft design was intended only to be a minimal check on safety.[38] Thus, there was no reason the manufacturer could not meet both the federal standards, and the standards set by state common-law, thereby permitting the state law based tort claims to go forward.[39]

Two additional cases further illustrate the point. In *Smith v. Atlantic Richfield Co.*,[40] a miner sued the operators of a coal mine in Utah for injuries sustained during a partial roof collapse.[41] In conformance with federal regulations, the roof plans for the mine were submitted and approved by the Mine Safety and Health Administration, the federal agency which oversees mine operations.[42] The defendants asserted this specific approval as a defense to the plaintiff's claims; nonetheless, the Tenth Circuit held that compliance with the regulation and agency approval were not conclusive of due care.[43] The court held that it was up to the jury to determine if the safety measures taken by the defendants to protect the miners were reasonable and prudent.[44]

In *Lubbock Manuf. Co. v. Perez*,[45] a wrongful death and personal injury suit was brought against the designer and manufacturer of a liquified petroleum gas transport vehicle which overturned and exploded.[46] The defendant asserted that its detailed plans and specifications for the design of the LPG trailer were approved by the Texas Railroad Commission as required by Texas statute, and thus, the trial court lacked the ability to adjudicate the appropriateness of the design.[47] The Texas court rejected this argument, and stated that neither the design approval by the Railroad Commission nor compliance with the statute established the defendant's due care in designing and manufacturing the vehicle.[48] Further, the court held that the legislative delegation to the Commission did not divest the court of the ability to independently assess the potential negligence of the design.[49]

The point of this discussion is not to say that compliance with statutes and regulations is irrelevant to the defense of common-law tort suits. Quite the contrary. Even when courts hold that compliance is not an absolute defense, they almost universally hold that the fact of compliance is admissible on the issue of the reasonableness of a defendant's conduct, and is at least evidence that the defendant exercised minimal due care.[50] In many cases, this may be sufficient to avoid liability entirely, or at least, serve to minimize the exposure to a judgment for

punitive damages. This is particularly true if the circumstances surrounding the claim show there was no exceptional hazard involved and that the incident giving rise to the claims was typical within the contemplation of the statute or regulation.[51] This exception to the "compliance is no defense" rule was endorsed by the Supreme Court in *Ives*,[52] and ultimately was incorporated into the RESTATEMENT rule.[53] Courts often overlook this aspect of the RESTATEMENT rule. This may be due, in part, to defendants' failure to raise the issue by presenting the total circumstances giving rise to a particular claim, and showing the court how these circumstances were typical of the type of factual situation contemplated by the statute or regulation.

This strategy was used by propane distributors and manufacturers in *Jones v. Hittle Service, Inc.*[54] successfully to defend against wrongful death claims resulting from a propane gas explosion. The explosion was the result of the decedent's inadvertent ignition of gas which accumulated within a storm cellar due to a leaking underground line.[55] The plaintiffs claimed the defendants failed to properly odorize the gas despite the stipulation that the gas had been odorized to the level required by the regulation promulgated by the Kansas State Fire Marshall.[56] By asserting that the circumstances surrounding the gas leak and explosion were typical of those contemplated by the odorization requirement, the defendants effectively shifted the burden of proof on this issue to the plaintiffs. When the plaintiffs could not show that special circumstances existed which would have put the defendants on notice that more odorant than usual would be required, the defendants' defense of compliance with the regulation and industry standards was conclusively established, thereby allowing the defendants to prevail.[57]

Results of these arguments can be unpredictable at best. For a defense strategy to succeed in persuading a court to depart from the traditional RESTATEMENT rule, the defendant must argue that: (1) the event giving rise to the claim was common place; (2) the applicable statute or regulation tightly controlled the defendant's conduct; (3) the event was of the type specifically contemplated by statute or regulation; and (4) the specific industry to which the defendant belongs was subject to the broad political control of a legislative or executive branch of the government.[58] Such an argument may be difficult to construct given the facts of some situations; nonetheless, it provides a defendant with the best possibility of avoiding liability based upon its compliance with the applicable statutes and regulations.

An issue which arises in cases involving state common-law tort claims based upon conduct prescribed by federal statute is that of pre-emption. The federal pre-emption doctrine is founded on the Supremacy clause of the United States Constitution, and allows federal law to predominate over state law on the same subject matter when they conflict.[59] The pre-emption doctrine differs from the defense of compliance in that, if the pre-emption doctrine applies to a claim asserted under state law, the claim cannot be asserted and must be dismissed.[60] The doctrine is beyond the scope of this discussion; however, it is important to note

that it applies to the petroleum industry due to the express pre-emption clauses included within numerous federal environmental laws.[61]

D. *COMPLIANCE WITH INDUSTRY STANDARDS*

Staying abreast of current and emerging standards in the industry and conforming operations to those of others in the field is a prudent business philosophy, not only for competitive reasons, but also to provide some measure of protection from tort liability. However, courts have demonstrated a reluctance to allow industries to have the sole voice in setting their own standards.[62] As a Texas Court of Appeals stated in the oilfield groundwater pollution case of *Brown v. Lundell*[63] in response to the defendant's plea that its operations were in accordance with the uniform custom in the industry - "[i]t is easily conceivable that 'customary practices' might of themselves be unlawful or unreasonable or include negligence."[64] Likewise, as Supreme Court Justice Holmes stated in the case of *Texas & Pacific Railway Co. v. Behymer*:[65]

> What usually is done may be evidence of what ought to be done, but what ought to be done is fixed by a standard of reasonable prudence, whether it is usually complied with or not.[66]

Thus, the preceding analysis of the rule of statutory compliance applies with equal force to the defense of compliance with industry standards. Such a plea in defense of tort liability does not bar recovery, but is admissible as evidence of the defendant's due care.[67] In addition, at least one commentator has argued that if a defendant operates within an industry that adopts its standards as establishing the proper norm for safety, and the defendant complied with these standards, it should be conclusive at least on the issue of the defendant's good faith, thereby eliminating the possibility of an award of punitive damages to the plaintiff.[68]

III. CONCLUSION -- A PLAN OF ACTION

This discussion is intended to serve as an admonition to the petroleum industry - when establishing budgets and protocols for environmental health and safety, do not focus solely on meeting the minimal requirements of the applicable statutes and regulations - take into consideration the standards for reasonable and prudent operations established by judicial decisions.

A reasonable measure of protection against liability for common-law tort suits only can be afforded by adequate research and forward-thinking policy decisions. Individual operators within the industry must educate themselves on common-law trends, not only in the jurisdictions where they operate, but across the entire nation. Once a new legal theory of recovery succeeds against one industry, its acceptance by courts tends to expand across jurisdictions to find application against entirely different industries. Thus, an expansive and creative view of the development of the law is required to anticipate which operational areas represent

an unacceptable exposure to liability. Only then can environmental health and safety management act to adjust these operations to protect against the undesired effects of successful tort claims.

REFERENCES

1. RESTATEMENT (SECOND) OF TORTS § 282 (1965) [hereinafter "RESTATEMENT"].

2. *Collingwood v. Gen. Elec. Real Estate Equities, Inc.*, 376 S.E.2d 425, 428 (N.C. 1989).

3. RESTATEMENT § 283; *Busby v. Quail Creek Golf and Country Club*, 885 P.2d 1326, 1329 (Okla. 1994); *Collingwood*, 376 S.E.2d at 428.

4. *Yampa Valley Elec. Assoc., Inc. v. Telecky*, 862 P.2d 252, 254 (Colo. 1993) (setting standard for electrical utility); *Kimery v. Public Service Co. of Okla.*, 622 P.2d 1066, 1071 (Okla. 1981) (same standard); *Blue Flame Gas, Inc. v. Van Hoose*, 679 P.2d 579, 588 (Colo. 1984) (setting standard for suppliers of propane gas).

5. *Id.*

6. *See* RESTATEMENT § 285.

7. *Smith v. Atlantic Richfield Co.*, 814 F.2d 1481, 1487 (10th Cir. 1987); *Yampa*, 862 P.2d at 258.

8. WILLIAM L. PROSSER, HANDBOOK OF THE LAW OF TORTS 200 (4th ed. 1971); *see also* RESTATEMENT § 286; *Yampa*, 862 P.2d at 255 n.3; *Carter v. Wm. Sommerville and Son, Inc.*, 584 S.W.2d 274, 278 (Tex. 1979).

9. 1 J.D. LEE & BARRY A. LINDAHL, MODERN TORT LAW: LIABILITY & LITIGATION 102 (Rev. ed. 1994); PROSSER, *supra* Note 8, at 201; *see also* RESTATEMENT § 288B.

10. *Id.*; *see also Busby*, 885 P.2d at 1329; *Yampa*, 862 P.2d at 255 n. 3; *Carter*, 584 S.W.2d at 278. Also note that the same rules have been held to apply to the violation of local regulations and ordinances. *See* PROSSER, *supra* Note 8, at 190; RESTATEMENT § 288B cmt. a; *Kimery v. Public Service Co. of Okla.*, 622 P.2d 1066, 1070 n. 3 (Okla. 1981).

11. RESTATEMENT § 286 cmt. d; *Rudes v. Gottschalk*, 324 S.W.2d 201, 204 (Tex. 1959).

12. *See* PROSSER, *supra* Note 8, at 191. This doctrine is best illustrated by the court in *Howsley v. Gilliam*, 517 S.W.2d 531 (Tex. 1975), which stated, "[u]nder the negligence per se doctrine, civil law will not condone behavior which does not at least meet the minimum standard for behavior set by penal statutes. Violation of a penal statute will thus result in civil liability as a matter of law." *Id.* at 533.

13. PROSSER, *supra* Note 8, at 200-01; RESTATEMENT § 288B cmt. b.

14. PROSSER, *supra* Note 8, at 203.

15. Paul Dueffert, *The Role of Regulatory Compliance in Tort Actions*, 26 Harv. J. on Legis. 175, 176 (1989); RESTATEMENT § 288C cmt. a; *see also Kirkendall v. Harbor Ins. Co.*, 698 F. Supp. 768, 779 (W.D. Ark. 1988), *aff'd*, 887 F.2d 857 (8th Cir. 1989); *Glynos v. Jagoda*, 819 P.2d 1202, 1205 (Kan. 1991); *Collingwood v. Gen. Elec. Real Estate Equities, Inc.*, 376 S.E.2d 425, 428 (N.C. 1989).

16. Dueffert, *supra* Note 15, at 176; *see also Howsley v. Gilliam*, 517 S.W.2d 531, 533 (Tex. 1975).

17. *Karl v. Burlington Northern R.R. Co.*, 880 F.2d 68, 76 (8th Cir. 1989) (stating that courts nationwide have adopted the RESTATEMENT standard).

18. RESTATEMENT § 288C.

19. *See* PROSSER, *supra* Note 8, at 203-04; LEE & LINDAHL, *supra* Note 9, at 104; *Fought v. Solce*, 821 S.W.2d 218 (Tex. App.-Houston [1st Dist.] 1991, writ denied) (comparing a physician's statutory duty to his common-law duty); *Roadway Express, Inc. v. Baty*, 114 P.2d 935, 937 (Okla. 1941) (holding that statutory duties do not abrogate common-law duties with respect to motor vehicle operation).

20. *See Attocknie v. Carpenter Manuf., Inc.*, 901 P.2d 221, 224 n. 3 (Okla. Ct. App. 1995); Dueffert, *supra* Note 15, at 177.

21. *See* Dueffert, *supra* Note 15, at 177.

22. *See* Dueffert, *supra* Note 15, at 177.

23. *See Int'l Paper Co. v. Ouellette*, 479 U.S. 481, 496, 107 S.Ct. 805, 814 (1987) (making the same observation about the common-law nuisance standards established by various states). The point is well-illustrated by the Supreme Court in *Grand Trunk Railway Co. v. Ives*, 144 U.S. 408, 12 S. Ct. 679 (1892), which stated:

> The terms "ordinary care," "reasonable prudence," and such like terms, as applied to the conduct and affairs of men, have a relative significance, and cannot be arbitrarily defined. What may be deemed ordinary care in one case may, under different surroundings and circumstances, be gross negligence.

Id. at 417, 683.

24. 144 U.S. 408, 12 S. Ct. 679 (1892). *Ives* involved a wrongful death suit brought against the defendant railroad for a collision at a street crossing in Detroit. *Id.* at 409, 680.

25. *See* Dueffert, *supra* Note 15, at 180.

26. *See* Dueffert, *supra* Note 15, at 180.

27. *See* Dueffert, *supra* Note 15, at 180.

28. *Ives*, 144 U.S. at 420-21, 12 S. Ct. at 684.

29. *See id.* at 421-22, 684. This is the view that was adopted by the drafters of RESTATEMENT § 288C. Dueffert, *supra* Note 15, at 181 n. 34. *See also* Discussion *infra* accompanying Notes 51 through 58.

30. *See, e.g., Easterwood v. CSX Transp., Inc.*, 933 F.2d 1548 (8th Cir. 1991), *cert. granted*, 112 S. Ct. 3024 (1992), *aff'd*, 113 S. Ct. 1732 (1993) (applying Section 288C in a wrongful death action under Georgia law for negligent crossing design); *Karl v. Burlington Northern R.R. Co.*, 880 F.2d 68 (8th Cir. 1989) (applying Section 288C in a personal injury action under Iowa law for an collision at a grade crossing); *So. Pacific Transp. v. Maga Trucking Co.*, 758 F. Supp. 608 (D. Nev. 1991) (applying Section 288C in a property damage counter-claim asserted under Nevada law against the railroad for negligent crossing design); *Koch v. So. Pacific Transp. Co.*, 547 P.2d 589, (Or. 1976) (applying Section 288C in a personal injury action under Oregon law).

31. *See Glynos v. Jagoda*, 819 P.2d 1202, 1210-11 (Kan. 1991) (holding that compliance with building codes at the time the apartment complex was constructed was no defense, particularly when the code was subsequently revised to address the particular safety hazard at issue, which placed the defendant on notice of a hazardous condition); *Collingwood v. Gen. Elec. Real Estate Equities, Inc.*, 376 S.E.2d 425 (N.C. 1989) (holding that even though evidence showed that the subject apartment complex complied with the state and local building codes, the codes were no more than minimums,

and compliance does not necessarily conclude that the actor was not negligent when it failed to take additional precautions).

32. *Lyon v. Ranger III*, 858 F.2d 22, 27, 30 (1st Cir. 1988) (holding under Massachusetts law that the craft operator could be found negligent, despite compliance with operational statutes).

33. *Yampa Valley Elec. Assoc., Inc. v. Telecky*, 862 P.2d 252, 257 (Colo. 1993) (holding that the fact the defendant constructed and maintained its power line in compliance with the national code is not dispositive of whether it was negligent in causing the plaintiff's death).

34. *See Blue Flame Gas, Inc. v. Van Hoose*, 679 P.2d 579, 590-91 (Colo. 1984) (holding in a suit for damages resulting from residential gas explosions on the theory of inadequate odorization, that compliance with the state regulations did not insulate the defendant supplier from liability for negligence or for supplying a defective product); *Jones v. Hittle Serv., Inc.*, 549 P.2d 1383, 1389 (Kan. 1976) (stating in a wrongful death action resulting from a gas explosion that the stipulation of the parties that the gas met the state Fire Marshall's regulations for odorization, alone, did not conclusively establish that the defendants were not negligent as a matter of law).

35. *See Attocknie v. Carpenter Mfg., Inc.*, 901 P.2d 221, 228 (Okla. Ct. App. 1995) (holding a suit for personal injuries suffered in a school bus wreck allegedly caused by the lack of seat belts for passengers, the court held the manufacturer's compliance with federal and state safety standards did not establish that the bus was not defectively designed as a matter of law); *Kidron, Inc. v. Carmona*, 665 S.2d 289, 290-291 & n. 1 (Fla. Dist. Ct. App. 1995) (holding in a wrongful death action the fact that the defendant truck manufacturer did not violate any statutes regarding the installation of rear "under ride" guards was not an absolute bar to tort liability).

36. Dueffert, *supra* Note 15, at 205.

37. 985 F.2d 1438 (10th Cir.), *cert. denied*, 114 S. Ct. 291 (1993).

38. *Cleveland*, 985 F.2d at 1445-46.

39. *Id.* at 1444-45.

40. 814 F.2d 1481 (10th Cir. 1987).

41. *Smith*, 814 F.2d at 1482.

42. *Id.* at 1483.

43. *Id.* at 1487.

44. *Id.*

45. 591 S.W.2d 907 (Tex. Civ. App.-Waco 1979, writ dism'd).

46. *Lubbock*, 591 S.W.2d at 911.

47. *Id.* at 914.

48. *Id.* at 915.

49. *Id.*

50. *See, e.g., Smith*, 814 F.2d at 1487; *Yampa Valley Elec. Assoc., Inc. v. Telecky*, 862 P.2d 252, 257 (Colo. 1993); *Glynos v. Jagoda*, 819 P.2d 1202, 1210 (Kan. 1991); *Collingwood v. Gen. Elec.*

Real Estate Equities, Inc., 376 S.E.2d 425, 428 (N.C. 1989); *Blue Flame Gas, Inc. v. Van Hoose*, 679 P.2d 579, 591 (Colo. 1984).

51. *See* PROSSER, *supra* Note 8, at 203-04; LEE & LINDAHL, *supra* Note 9, at 47; *see, e.g., Jones v. Hittle Serv., Inc.*, 549 P.2d 1383, 1390 (Kan. 1976) (holding that compliance may be conclusive of due care in the absence of a showing of special circumstances).

52. *See* Discussion *supra* accompanying Note 89.

53. Comment "a" to RESTATEMENT § 288C provides:

> Where there are no such special circumstances, the minimum standard prescribed by the legislation or regulation may be accepted by the triers of fact; or by the court as a matter of law, as sufficient for the occasion; but if for any reason a reasonable man would have taken additional precautions, the provision does not preclude a finding that the actor should do so.

54. 549 P.2d 1383 (Kan. 1976).

55. *Id.* at 1387-88.

56. *Id.* at 1388-89.

57. *Id.* at 1391.

58. Dueffert, *supra* Note 15, at 215.

59. 2 MICHAEL DORE, LAW OF TOXIC TORTS § 11.07[1] (1996).

60. *See Wood v. General Motors Corp.*, 865 F.2d 395, 417 (1st Cir. 1988), *cert. denied*, 110 S. Ct. 1781 (1990).

61. *Nat'l Audubon Soc. v. Dept. of Water*, 869 F.2d 1196 (9th Cir. 1989) (addressing pre-emption of federal common-law nuisance claims under the Clean Air Act and the Water Pollution Control Act); *Int'l Paper Co. v. Ouellette*, 107 S.Ct. 805 (1987) (addressing pre-emption of state common-law nuisance claims under the Clean Water Act).

62. *See, e.g., Kirkendall v. Harbor Ins. Co.*, 698 F. Supp. 768, 779 (W.D. Ark. 1988), *aff'd*, 887 F.2d 857 (8th Cir. 1989).

63. 334 S.W.2d 616 (Tex. Civ. App.-Amarillo, 1960), *aff'd*, 344 S.W.2d 863 (Tex. 1961).

64. *Brown*, 334 S.W.2d at 619.

65. 189 U.S. 468, 23 S.Ct. 622 (1903).

66. *Id.* at 470, 623.

67. *See, e.g., Kirkendall*, 698 F. Supp. at 779 (involving the operation of blood banks and stating that compliance with a *de facto* industry standard does not necessarily insulate a defendant from liability); *Yampa Valley Elec. Assoc., Inc. v. Telecky*, 862 P.2d 252, 257 (Colo. 1993) (involving the electrical utility industry and applying the same rule); *Glynos v. Jagoda*, 819 P.2d 1202, 1210 (Kan. 1991) (involving the building design and construction business and stating that while compliance with industry standards may be evidence of due care, it does not preclude a finding of negligence where a reasonable person would have taken additional precautions under the circumstances); *Jones v. Hittle Serv., Inc.*, 549 P.2d 1383, 1390 (Kan. 1976) (involving the propane distribution industry and stating that customary practices are not necessarily due care); *Brown v. Lundell*, 334 S.W.2d 616, 618-19

(Tex. Civ. App.-Amarillo, 1960), *aff'd*, 344 S.W.2d 863 (Tex. 1961) (involving oil and gas industry and stating that conformance to the general practice or custom would not excuse the defendant's failure unless it was consistent with due care).

68. Dueffert, *supra* Note 15 at 199-200.

The ISO 14000 Environmental Management Standards: An Alternative to "Command and Control"?

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Abstract:

"A company that registers to ISO 14001 should never see a regulator again."
- James Seif, Secretary
Pennsylvania Dept. of
Environmental Protection

The above statement is a strong endorsement for an emerging set of voluntary standards, by one of the nations top state environmental regulators. The U.S. EPA also sees adoption of the ISO 14000 standards by industry as a means of leveraging its dwindling enforcement resources for even greater environmental protection. Why were these standards created? Why are companies beginning to use them even before they are officially published, and what are the perceived benefits? Why are they being used by foreign governments when U.S. exploration and production companies want to drill? And how can this "systems approach" provide assurance of greater environmental protection than the traditional "Command and Control" strategy used by U.S. regulatory agencies for the past 25 years? The presenter will answer these questions as he demonstrates the compatibility of ISO 14001 with modern business and quality management practices.

"A company that adopts ISO 14001 should never see a regulator again." These words, said before the US Technical Advisory Group developing the ISO 14000 series of environmental standards, came from a surprising source - they were spoken by James Seif, head of the Pennsylvania Department of Environmental Protection. He was not suggesting that state and federal regulators would soon need to find other employment, but he was expressing confidence that the ISO 14001 environmental management system model could provide sufficient assurance of environmetal protection to perhaps be considered an alternative to the "command and control" regulatory track.

How could such a small document (the ISO 14001 specification, which contains all the requirements for a certifiable environmental management system, has less than 20 pages of text, including its informative annex) have as much impact as tens of thousands of pages of regulations?

First, the system does not replace environmental regulations, but provides a management framework to assure compliance with whatever regulations are applicable, wherever in the world the environmental management system (EMS) exists. It provides this assurance in the same way, and using the same types of system elements, that well-run companies use to control the quality of their products, production costs, and all other aspects of their business.

In the business world, management commits to running its business in a certain fashion, setting a level of performance, in "mission" and "vision" statements. The organization assesses its current status, then sets goals consistent with its vision, and develops an action plan to achieve these goals. The organization tracks its performance, and takes corrective action, if things are not going according to plan. Lastly, management periodically reviews the organization's performance, the plan, including its goals, and perhaps even its mission and vision, and makes change decisions based upon the evidence and changing circumstances. This is often done during the budgeting or "rolling forecast" process.

Thousands of companies that have adopted Total Quality Management (TQM) systems, including those with quality systems certified to the ISO 9000 standards attest to the efficacy of the management system. The ability of the EMS to assure more consistent and efficient regulatory compliance can be explained by examining how companies have altered their approach to quality management over the last decade, to assure more consistent product quality and more efficient operations.

Fifteen years ago, the world of the quality professional was focused on the end of the production line: sampling, analysis and acceptance or rejection of output, based on the analytical results. Although a workable method of assuring

product quality, it was not foolproof. Errors in sampling or analyses regularly led to customers receiving a product that did not meet their requirements.

Operations surmised that, given the uncertainties of the end-of-line focus, that if less off-spec product came off the end of the line, less would be inadvertently shipped to the customer. Thus, focus shifted upstream, to the manufacturing process itself, starting with acceptance by top management and the line organization of their responsibility for product quality. Individual employees began buying into the quality process and contributing ideas for quality improvements. Many companies adopted a system for quality management, based on the principle that continuous quality improvement meant nothing more than meeting customer requirements a greater percentage of the time.

The elements of the adopted quality systems were designed to control every aspect of the manufacturing process to assure product consistency. Management and employees, line and staff functions alike, were part of this quality system, as were the processes, procedures and resources for implementing quality management. The essential elements of the system which contributed to more consistent product quality were:

1. Management commitment to quality, including providing the necessary resources, human and other, to meet customer requirements and other objectives for quality.

2. A process for determining customer requirements, and the company's ability to meet those requirements before entering into a contract.

3. A process to disseminate those customer requirements to everyone in the organization who needs to have such information.

4. Provision of sufficient procedures, equipment, instrumentation, specifications and maintenance to ensure the manufacturing process is controlled.

5. Sufficient training for employees associated with these controlled processes, so that the established procedures are followed consistently employee-to-employee and shift-to-shift.

6. The ability to determine when something has gone awry, and the means to prevent any resultant off-spec product from getting to the customer without customer knowledge.

7. Procedures for implementing corrective and preventive action to eliminate the causes of actual and potential "nonconformities", or departures from requirements.

8. A process for taking and maintaining records, as evidence that work was performed, procedures were followed and requirements were met.

9. And lastly, a process for internal auditing and management review, to verify that quality activities and results are going according to plan, and to determine the effectiveness of the quality system.

Once companies got their own houses in order, their focus shifted even further upstream, to their raw material suppliers, with many requiring suppliers to have a quality system in place. The objective was to obtain raw materials with less variation in quality, thus reducing variation in the final product. Before the widespread acceptance of the ISO 9001 quality system standard, companies with formal TQM systems were regularly auditing their suppliers to confirm that essential quality system elements had been implemented. Many companies have since found it much more expedient to require, or at least encourage, their key suppliers to conform to the ISO quality standard, a standard which contains all those essential elements, than to maintain an intensive supplier quality auditing practice.

Like the quality professional of old, the environmental professional's focus is still on the end of the pipe or stack, not on the process, but the new standards may change all this. The ISO 14001 standard describes a model EMS containing all of the elements listed above, thus assuring compliance with environmental regulations in the same manner that ISO 9001 assures conformance to customer requirements.

In the ISO 14000 EMS, the organization's top management must specifically commit to compliance with applicable environmental laws and regulations in the environmental policy. This compels management and the line organization to accept responsibility for environmental compliance, to rank it among its organizational priorities and to demonstrate its commitment through policy implementation.

Just as the quality system requires the organization to determine customer requirements, and communicate them to all who need to know, ISO 14001 requires a process to determine legal requirements, and communicate them appropriately within the organization. The ISO 14001 EMS further requires that a periodic evaluation be made of compliance with applicable environmental laws and regulations. This makes good sense: management has committed to compliance, therefore the organization should periodically check to see how it is doing. And when a departure from plans or other requirements, including regulatory compliance, is sensed, the corrective action feature of the system must "kick in", to get the organization back on track.

Lastly, the EMS is regularly audited, to be sure that all the essential elements are in place, and management conducts periodic reviews to make sure the system is operating effectively. These activities not only provide further assurance of compliance with environmental regulation, but also drive continuous improvement of the EMS, resulting in enhancement of environmental performance beyond the level required by regulation.

Besides internal auditing and management review, a mechanism has been established to obtain independent, objective certification that an EMS contains all the required elements, including commitment to compliance, operational control, corrective action, internal auditing and management review, and has been fully implemented. About 65 companies in the United States offer this certification, or registration, service for the ISO 9000 quality standards, and there is strong indication that most will offer ISO 14001 EMS registration services, as well.

With such assurance of conformance to requirements, including regulatory requirements, built-in throughout the system, plus objective third-party review, government regulators can focus on setting policy and more carefully scrutinizing those organizations without an EMS. Thus the agencies' resources will be leveraged by the registrars, and by the regulated community, itself. US exploration and production companies drilling overseas have already begun to see requirements that they have an effective EMS in place. These foreign governments, many of which have a complete framework of environmental regulations, but little or no enforcement capabilities, are beginning to realize the power of the systems approach.

In summary, assurance takes place because top management must commit to regulatory compliance as well as pollution prevention, and demonstrate this commitment through implementation of environmental policy. Additionally, management must provide the necessary resources to assure EMS effectiveness, especially when corrective action is necessary. Most significantly, this "top-down" approach compels everyone in the organization to recognize his or her role in assuring environmental protection, to act upon that recognition, according to a plan, with documented procedures and training, and to participate in the continuous improvement process.

Thus, a little document becomes a powerful tool, by describing an environmental management system which mandates that environmental regulations be regarded in the same way as customer requirements in the quality system. ISO 14001 turns the primary focus of environmental management away from the end of the pipe, or stack and places it on the process itself. Less pollution, waste and energy usage can reasonably be expected to result, as well as more consistent operation of environmental control devices and greater assurance of environmental performance that meets or exceeds regulatory requirements.

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Risk-Based Corrective Action at Petroleum Sites in Oklahoma - Issues, Methods, and Applications

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Abstract:

The State of Oklahoma has adopted a Risk-Based Corrective Action (RBCA) method of dealing with petroleum leaks and spills. The RBCA method, based on ASTM Standard E1739 (1995), represents a major change in philosophy for decision making and management at petroleum spill sites. The risk-based corrective action program establishes step-by-step procedures to determine data needs, initial remedial actions, site cleanup criteria, target cleanup levels, site-specific corrective actions, site closure criteria, monitoring plans, and the use of natural attenuation as a site management tool. These procedures involve estimation, modeling, professional judgment, and uncertainty. The RBCA process uses a tiered approach which progresses from conservative default assumptions in Tier 1 to more site-specific calculations in Tiers 2 and 3. The RBCA process has been modified and applied to underground storage tank (UST) regulations in Oklahoma. Oklahoma RBCA (ORBCA) includes a "Tier 1a" option which allows for some site-specific calculations in the Tier 1 assessment. Certified UST consultants in Oklahoma are required to attend a three day ORBCA training course. The authors have been involved in teaching ORBCA training courses which explain the ORBCA process and also teach fate and transport, risk assessment and toxicology principles. This paper introduces the RBCA process, outlines how the RBCA process is being implemented in Oklahoma, discusses several issues related to petroleum release sites and the RBCA processes, and makes recommendations.

INTRODUCTION

Petroleum hydrocarbon contamination in the subsurface from petroleum hydrocarbon sites and leaking underground storage tanks (USTs) is one of the most important environmental issues that our nation faces. Nationally there are over 1.2 million UST sites, with approximately 12,000 in Oklahoma. Approximately 400,000 USTs have been upgraded nationally to 1998 USEPA standards. As these tanks are replaced and upgraded, new releases are discovered. Presently there are over 250,000 confirmed releases at these sites with approximately 1000 new cases being reported each week.

The economic impact of remediating these sites in a limited time span is severe. With groundwater remediation of a site typically costing between $100,000 and $1 million dollars, it is projected that state funding will cover only 6% of remediation costs nationally and 7.5% in Oklahoma (1). Even the most expensive remediation systems are rarely able to clean up a site to drinking water standards or to other state-mandated category levels. As a result, new technologies, approaches, and methods are being sought to deal with this substantial undertaking.

The challenges faced in dealing with the magnitude of petroleum hydrocarbon cleanup raise several pertinent questions: Are present standards required to ensure public health and safety? Are the resources available to meet the demand? Do we have the technology available to meet the demand? What are the financial restraints on corrective action? What about property transactions and insurance?

It is clear that the cost associated with remediating petroleum hydrocarbon release sites to existing standards are tremendous. The Oklahoma Corporation Commission (OCC), which regulates petroleum sites in Oklahoma, has concluded that "the traditional approach of treating all sites equal and requiring every site to be remediated to nondetect or other empirically derived levels is technically and economically unfeasible" (2). It is desirable, therefore, to prioritize sites so that the available money is used to clean up sites which pose actual risks to human health. To provide a uniform approach to assessing human health risk and making corrective action decisions at petroleum release sites, the American Society of Testing of Materials (ASTM) formulated the standard *Risk Based Corrective Action Applied at Petroleum Release Sites, Standard E 1739* (3). The ASTM E 1739 document, referred to by the acronym "RBCA", was developed by a multifunctional and multidisciplinary committee of regulators, hydrogeologists, engineers, scientists, and modelers.

The RBCA process is designed to provide a decision making process that protects human health and the environment, is consistent and technically defensible, and is practical and cost effective. It incorporates a tiered approach

which progresses from conservative default assumptions in Tier 1 to more site-specific calculations in Tiers 2 and 3. The ASTM RBCA standard is intended to serve as a framework from which states can build their own regulations and policies. The OCC used the ASTM standard to develop Oklahoma RBCA (ORBCA). ORBCA is based on the RBCA framework, but does include a Tier 1a option which allows for more site specific information to be incorporated in the Tier 1 assessment.

THE RBCA PROCESS

The RBCA process is a tiered approach in which each successive tier involves more thorough investigation and the use of more site-specific parameters for analysis. Figure 1 shows a flow chart of the RBCA process. The ASTM RBCA standard defines the process in clear steps, but frequently mentions ways to be flexible with the process and also emphasizes that the standard is to serve as a guideline.

In RBCA, site specific chemical concentrations at the site are compared with concentrations that represent unacceptable risks. If concentrations at the site are less than those corresponding to unacceptable risks, then the site can be closed. This is the reverse mode of risk assessment. In a conventional risk assessment, risks are calculated based on site concentrations and then compared to unacceptable risks. In RBCA, the unacceptable risks are used to back calculate corresponding acceptable concentrations and then compared to site concentrations.

The purpose of the initial site assessment is to determine the source and severity of contamination, and to identify potential risk receptors and possible transport pathways. The site assessment involves a site inspection, an examination of site history and records, the installation of boreholes and monitoring wells, and limited sampling of soil and groundwater. Based on the site assessment, the urgency of initial response is classified according to pre-determined guidelines. The site assessment also provides data for the Tier 1 evaluation.

In the Tier 1 analysis, the reasonable potential exposure scenarios are selected from a list of predefined exposure scenarios. For each compound and selected exposure scenario, Tier 1 Risk Based Screening Level (RBSL), "Look-Up Tables", are used to select the appropriate RBSLs. The RBSLs are concentrations in affected media which result in unacceptable risk levels. For example, a RBSL in soil for enclosed space vapor inhalation pathway concerns contaminated soils beneath a building and resulting vapor intrusion into the building. The RBSL in this case represents a soil concentration which would result in interior air concentrations that correspond to unacceptable risk. Because

exposures vary between receptors, there can be different RBSLs for different receptors (e.g., residents, commercial workers, children) as well as for different exposure pathways. The ASTM RBCA standard contains RBSL tables which have been developed using analytical models with conservative default parameters for contaminant transport, toxicology, and exposure (using a "reasonable maximum exposure"). These tables are intended by ASTM to serve only as an example; however, some states have adopted these tables directly, while others like Oklahoma have modified the Tier I results to conform to their specific needs.

For the Tier 1 assessment, site concentrations are compared to the appropriate RBSLs. If all concentrations are below the applicable RBSLs, then the site can proceed to compliance monitoring or closure. If a concentration exceeds the appropriate RBSL, the decision makers can choose to perform remediation or to perform a Tier 2 evaluation. Two remediation options are available. If remediation to Tier 1 RBSLs is practicable, a full corrective action program can be undertaken. The other option is interim remediation which involves partial source removal or other actions to reduce risks followed by reclassification and reevaluation.

In Tier 2, additional site data is collected to more clearly define the contamination, the transport pathways, and the exposure at the site. Tier 2 allows the option for negotiating site-specific cleanup goals and points of compliance. The methodology used in developing RBSLs can be used with site-specific parameters to determine Site Specific Target Levels (SSTLs). The development of SSTLs may involve the use of site specific fate and transport modeling. The amount of data accumulated at the site will dictate the type of modeling used for this analysis (usually analytical). Concentrations at the site are then compared to the SSTLs. If concentrations are below the SSTLs, the site can proceed to compliance monitoring or site closure. If SSTLs are exceeded, three options - interim corrective action, final corrective action, or tier upgrade to Tier 3.

Tier 3 involves an expanded site assessment to obtain additional site specific input parameters for the use of more sophisticated statistical and contaminant fate and transport models. Tier 3 analyses may involve more thorough and more costly data collection and modeling efforts than the Tier II. These analyses could include numerical ground water flow and transport models, statistical techniques such as Monte Carlo techniques, and data gathering to determine biodegradation rates and other transport and fate parameters. New SSTL values are chosen based on the results of the modeling efforts. If source concentrations do not exceed Tier 3 SSTLs, no further action may be required. If remediation is required, again either an interim corrective action can be performed followed by review, or a final corrective action program may be designed and implemented. The corrective action program may include some combination of

source removal, treatment, and containment technologies, as well as institutional controls.

OKLAHOMA RBCA

In the past, the OCC had relied on drinking water standards to determine clean-up levels for UST sites. UST sites were classified into one of three categories based on several risk factors. The OCC has allowed or requested consultants to perform risk assessments for certain sites. In a risk assessment, the total risks to potential receptors are computed and compared to unacceptable risk levels (maximum cancer risk of 10^{-5} recommended by *Risk Assessment Guidance Document,* (4)). If the calculated risks from a site are below unacceptable levels, the case may be closed.

The Oklahoma RBCA (ORBCA) regulations for UST sites, are a modification and application of ASTM RBCA. Oklahoma's *Risk-Based Corrective Action Guidance Document* (2) was developed by the OCC in conjunction with a multifunctional and multidisciplinary stakeholders committee of regulators, hydrogeologists, engineers, scientists, and modelers. The ORBCA process gives a more consistent, uniform, and directed methodology for assessing risks at a site than did the previous regulations. In ORBCA, all transport and exposure parameters in Tier 1 are default values which have already been chosen and the results are tabulated in RBSL look-up tables.

A flow-chart of the ORBCA process is shown in Figure 2. The opening of a case on a site is triggered by the suspicion of a release. A preliminary release investigation confirms the release with one well or with two tank tightness failures and the results are submitted in 20 day report. The case can be closed at this point based on stringent category levels, otherwise a Tier 1 site assessment is performed.

The ORBCA Tier 1 site assessment is similar to that described for RBCA and involves the installation of four monitoring wells. Tier 1 RBSLs are calculated with a risk of 10^{-6} for present receptors and 10^{-4} for construction workers and future receptors. A future receptor has been defined as a receptor which is not yet present at the site, for example the possibility that a drinking water well may be installed in the future. The RBSLs for ground water exposure routes are a function of the distance from the location of the source or the sampling point to the receptor using a dilution attenuation factor (DAF) calculated with an analytical ground water model. The measured concentrations at the site are compared with the appropriate RBSLs. The Tier 1 process can be presented and comparisons to RBSLs performed using a set of preconstructed Excel® worksheets.

If the concentrations at the site are above the Tier 1 RBSLs, a Tier 1a analysis may be performed. In the Tier 1a analysis, some site specific fate and transport information can be used to modify the Tier 1 RBSLs. For example, the depth to ground water at the site may be deeper than the Tier 1 default value. As a result, Tier 1a RBSLs may indicate that the existing site concentrations are acceptable. Closure may be pursued before going to a more detailed Tier 2 analysis. A report is then submitted to the OCC presenting the results of any Tier 1a analysis. Although the consultant recommends what action should be taken as the result of the ORBCA analysis, the regulations require that OCC review and comment on the results. There are four options for action based on the Tier 1 assessment - no action, final corrective action, interim corrective action, and tier upgrade (Tier 2 analysis).

A Tier 2 analysis requires additional site investigation which may include the installation of more wells, determination of hydraulic conductivity, and air compliance monitoring among other information. The models used to develop the Tier 1 RBSLs may be used in Tier 2, and/or additional models may be used. The OCC has the right to review software and models before making decisions. The models are used with the site-specific data to calculate Tier 2 SSTLs. Site specific concentrations are then compared to the SSTLs. A report is submitted to the OCC and a decision is made on which of the four options to select - no action, final corrective action, interim corrective action, and tier upgrade (Tier 3 analysis). The Tier II analysis is unchanged from the RBCA recommended process.

ISSUES

Many issues are addressed through the RBCA/ORBCA process. However, several important issues remain. These include:

- public perception of risk management;
- future land use uncertainty and the evaluation and control of future risks;
- real estate, insurance, and legal issues;
- remediation technologies; and
- evaluation of intrinsic remediation for the no action alternative.

The public perception of risk management at petroleum hydrocarbon release sites will be key to the success of the RBCA process. Integrated into this complex issue is the question "how clean is clean?". What level of contaminant removal is acceptable? The RBCA process is based on the principle of site specific clean up levels. Site clean up levels are determined on potential risk to

receptors at that specific site. As a result, if there are no potential receptors, relatively high concentrations of targeted chemicals may remain in the subsurface at the site and yet be protective of human health and the environment. The public, however, may not perceive it that way and emphasize the uncertainties in the assessment.

One of the uncertainties is potential future land use. Although the RBCA process is based on technically defensible principles, the determination of future land use is not absolute. A future potential pathway can be considered at a site and a RBSL or SSTL can be established based on a less stringent risk - 10^{-4} rather than 10^{-6} (2,3). The OCC requires that all impacted parties be notified by certified mail. In addition, the OCC plans to register with the Oklahoma Water Resources Board all sites on which the RBCA process was used for site closure. If this is successful, the Water Resources Board would be responsible for ensuring that future water wells are not impacted by petroleum hydrocarbon releases. Other potential mechanisms for control of future exposure include institutional controls such as deed restriction of impacted properties. At present, the OCC does not have authority for such institutional controls. This could be a viable method of control but could also have significant economic ramifications.

A major concern surrounding petroleum release sites is the potential for devaluation of real estate and the potential for lawsuits. In order to minimize this, it is the responsibility of the regulatory body and consultants to ensure that due diligence is performed and all options considered. In addition, educating all involved parties could minimize future misconceptions and lawsuits. Because this process is scientifically based, the general public may not understand the ramifications without education from the regulators and consultants.

Under risk-based cleanups, it is likely that the entire site will not need to be cleaned up to drinking water or other stringent standards. Instead, source removal or other actions may be taken to eliminate risks. This changes the focus of remediation technologies. As a result, consultants and regulators may need to change their standard practices and re-evaluate their approach to remediation.

At some sites, the best approach may be to do nothing and allow "intrinsic remediation" to reduce contaminant concentrations at the site. The use of intrinsic remediation and monitoring along with institutional controls may allow a site to be closed (5). However, the evaluation and prediction of intrinsic remediation is a matter of considerable scientific research and debate. Standard methods and policies dealing with intrinsic remediation need to be developed.

CASE STUDY

The purpose of this case study is to compare the results of RBCA and ORBCA tier 1 analyses with Oklahoma's previous standards. In order to do so actual data from a UST site in Oklahoma was utilized (for illustrative purposes a groundwater well was added) . Refer to Figure 3 for a site layout map. Site specific information is tabulated in Tables 1 and 2. This information was utilized to determine RBCA and ORBCA tier 1 (and tier 1a) RBSLs. The results are tabulated and compared in Table 3.

As indicated by the results, much of the conservatism associated with the RBCA process has been removed from the ORBCA evaluation. The ORBCA process has allowances for attenuation factors to incorporate distances to groundwater receptors. In addition, the ORBCA vapor transport models have been modified to be less conservative. The results is that the ORBCA results incorporate more site specific data in Tier 1 and can yield less stringent cleanup levels.

RECOMMENDATIONS

The authors make the following recommendations:

- Maintain public participation. The RBCA process allows some sites to be closed while they still have elevated chemical concentrations. It is important that the public be informed and educated about the risks (or lack of risks) at a site to avoid misconceptions and unwarranted controversy.
- Educate consultants and regulators. In order to make responsible evaluations and decisions, consultants and regulators need to not only understand the RBCA process, but also have a firm grasp on the science which goes into the risk assessment process. Specifically they need to understand fate and transport processes for petroleum hydrocarbons. The authors have been involved in teaching short courses which explain the RBCA process and also teach fate and transport, risk assessment and toxicology principles. We feel that this knowledge is key to making proper predictions, evaluations, and decisions.
- Educate those in the real estate, insurance, and legal sectors about RBCA. Those involved in the non-technical fields which can be affected by petroleum release sites need to understand the RBCA process, its advantages, and its implications.

- Establish procedures and policies for evaluating and predicting intrinsic remediation. There is a need to develop standard practices which are consistent, technically defensible, practical, and cost effective.

REFERENCES

1. Gurr, T.M., and Homann, R.L., "Managing Underground", *Pollution Engineering*, pp. 40-44 (1996), May.
2. Oklahoma Corporation Commission, *Risk-Based Corrective Action Guidance Document*, (1996).
3. American Society of Testing of Materials, *Risk Based Corrective Action Applied at Petroleum Release Sites, Standard E* 1739, (1995).
4. Oklahoma Corporation Commission, *Risk Assessment Guidance Document,* (1994).
5. Hicks, R.T., and Rizvi, R., "Do-Nothing Cleanups", *Civil Engineering*, pp. 54-57 (1996), September.

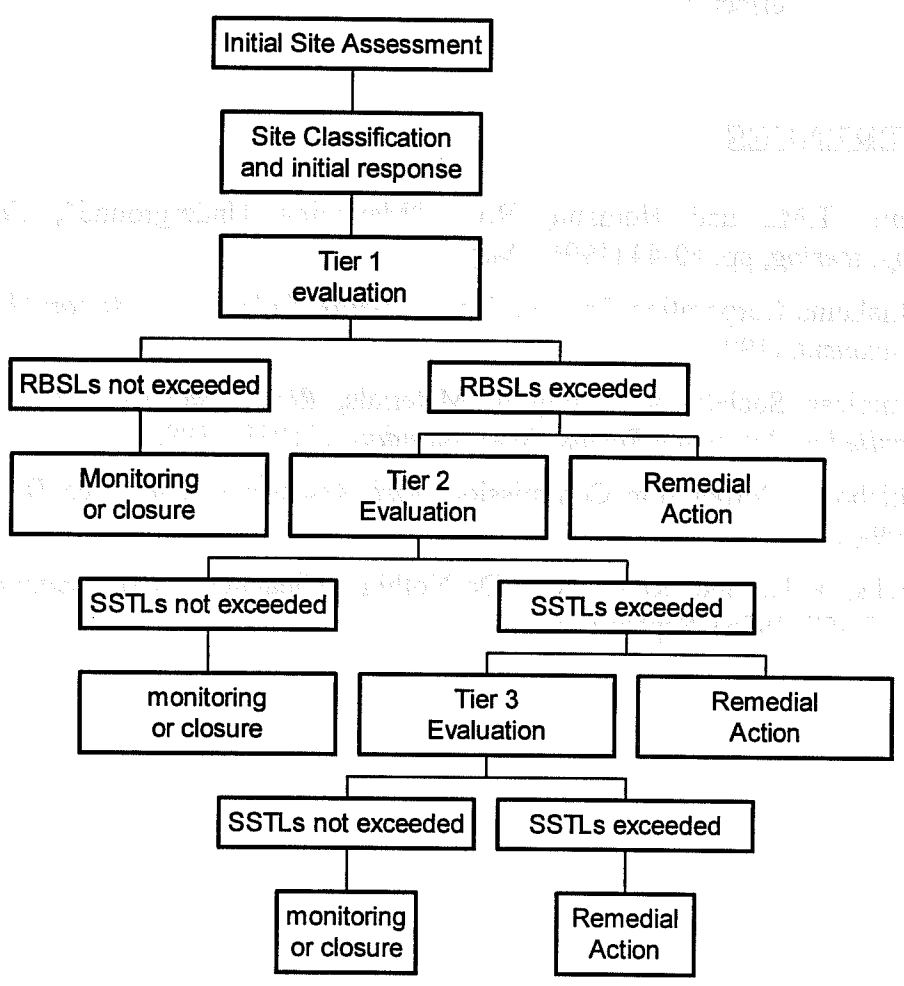

Figure 1 RBCA Flow Chart

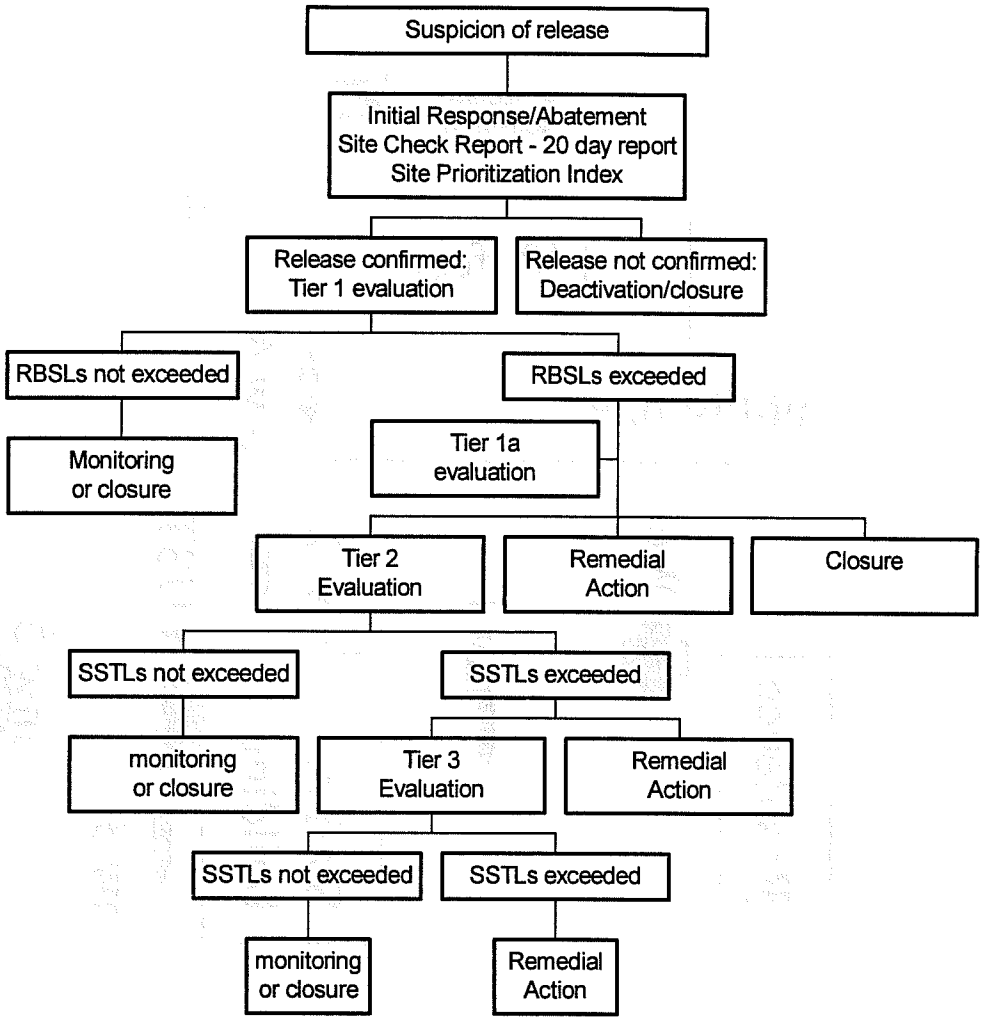

Figure 2 ORBCA Flow Chart

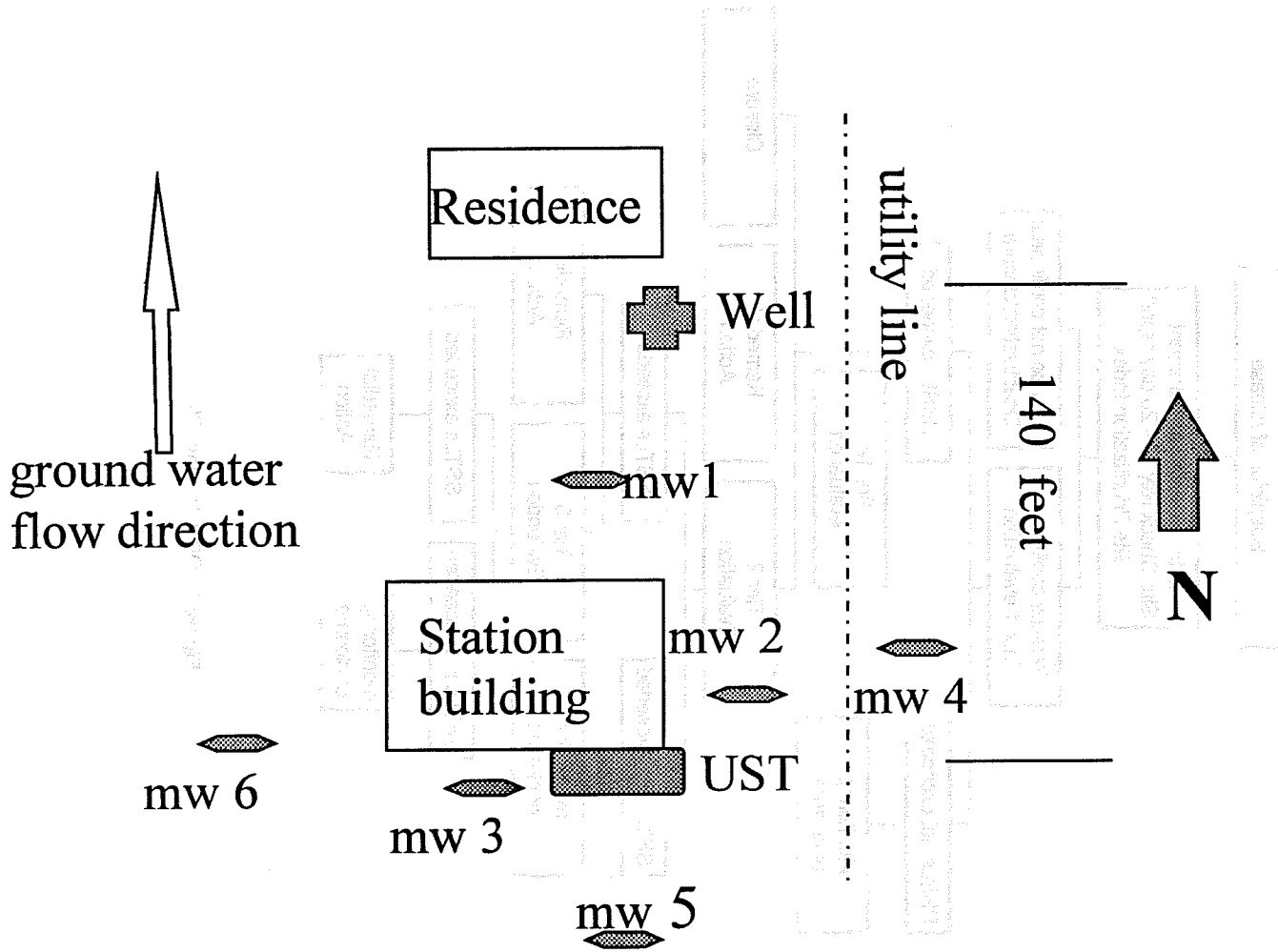

Figure 3: Case Study Map

Table 1 Site Specific Information	
Depth to Groundwater	5 Feet
Lithology	Clayey Silt to 10', Underlain by Fractured Shale
Well Screened Interval	Unknown
Station Age	20 Years
Hydraulic Conductivity	0.1 Ft/Day
Hydraulic Gradient	0.05 Ft/Ft
Fraction of Organic Content	0.003

Table 2 Well Information		
Well	Benzene in Soil (mg/kg)	Benzene in GW (mg/l)
MW -1	ND	ND
MW -2	12 mg/kg	3 mg/l
MW -3	20 mg/kg	4 mg/l
MW -4	ND	ND
MW -5	ND	ND
MW -6	ND	ND

ND = Non-detect

Table 3

Comparison of Tier 1 Cleanup Levels (Benzene)

Pathway	Receptor	Target risk	Former Category System		ORBCA* Analysis Tier 1		RBCA** Analysis Tier 1	
			Soil mg/kg	GW mg/l	Soil mg/kg	GW mg/l	Soil mg/kg	GW mg/l
Ground water injestion	resident adult	1.00E-06	5 mg/kg	.05 mg/l	0.28	0.017	0.0172	0.00238
	resident child	1.00E-06	5 mg/kg	.05 mg/l	0.59	0.037	0.0172	0.00238
Dermal contact/Inhalation	utility worker	1.00E-04	5 mg/kg	.05 mg/l	923.3	557.6	1000	>S
Soil and Ground water vapors	comercial worker	1.00E-06	5 mg/kg	.05 mg/l	1.69	3.84	0.011	0.0739

* ORBCA Guidance Document, 1996

** ASTM E 1739

(distance to grounwater receptor set at 100 feet for the ORBCA results)

>S= greater than solubilty

Using Remote Sensing for Assessing Environmental Damage in Oil and Gas Exploration

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For exploration and production activities, remote sensing can be used to accurately and quickly determine environmental damage, whether pre-existing or due to historical production activities. Examples of environmental damage assessment projects that can benefit from remote sensing are oilfield transaction audits, baseline environmental assessments of lease blocks, and monitoring the effects of surface disposal of produced water. Walsh Environmental Scientists & Engineers has used remote sensing for oilfield damage assessment since 1992. This paper describes the techniques we have developed and their applications. In this paper, remote sensing is defined as the use of a Geographic Information System (GIS) to view and analyze data from satellite images and aerial photographs.

TYPES OF ENVIRONMENTAL IMPACTS IN PRODUCING FIELDS SUITABLE FOR REMOTE SENSING

Many types of environmental impacts exist in producing fields, as listed in Table 1. Remote sensing isn't able to determine all of the impacts listed in Table 1 -- impacted ground water, for example, normally is not expressed on the surface -- but it is helpful in many cases. The impacts that can be addressed by remote sensing include oil spills, devegetation, erosion, and impacts from surface disposal of produced water.

COMMON SITUATIONS WHERE REMOTE SENSING CAN HELP

Remote sensing is beneficial in the following situations:

Remote and inaccessible areas: In rainforests and other remote areas, remote sensing may be the only way to adequately view the producing field and surrounding area. In rainforests and tundra, for example, surface travel is difficult and often damaging to the environment.

Large area to cover: In large fields, remote sensing allows rapid viewing of hundreds of wells and/or hectares quickly. Remote sensing can be used to prioritize areas for ground visits.

Short time frame: Similarly, when time is short due to bidding restrictions, etc., remote sensing can be used to generate a first pass evaluation of environmental damage that can later be refined into an audit if required.

Historical viewpoint needed: Archived satellite and aerial photograph imagery can be valuable. One oil company operating in South America had entered a lease in 1985 and hadn't inventoried environmental damage at the time. By using historical satellite imagery from 1985, we quantified the amount of deforestation (the principal impact in this Amazon rainforest block) at the time of the lease transaction, providing baseline information 10 years later. For another client, we have used historical aerial photographs to determine the locations of buildings and facilities that no longer exist.

WHY USE REMOTE SENSING FOR ENVIRONMENTAL DAMAGE ASSESSMENT?

In addition to the situations mentioned above, there are additional benefits of remote sensing:

Inexpensive: When auditing a 400-well field, for example, remote sensing can be significantly less expensive than having field teams visit each wellhead.

Visual documentation: When used by itself or in conjunction with field studies, remote sensing provides visual documentation that is easily understood.

Quantification: Remote sensing can easily determine the areal extent of spills, deforestation, and other environmental concerns. This is often much more difficult on the ground, requiring surveys, etc. Recalculation in hectares, acres, square meters, or square feet is also easy.

TECHNOLOGIES USED

WALSH uses four key technologies in our remote sensing damage assessments: GIS software to manipulate images, digital satellite imagery, digital aerial photography, and a Global Positioning System (GPS) for ground truthing.

GIS Software: GIS software is used to manipulate and analyze various data involved in damage assessments. Visual images, including satellite images and aerial photographs, are imported into the GIS, then georeferenced. Georeferencing is the correction of the distortion that is inherent in all images, and is done based on surveyed data from maps, GPS surveys, and other sources. The georectified satellite or aerial photograph images form the "basemap" for overlaying engineering drawings of oilfield infrastructure including production facilities and well locations.

The GIS software is then used to analyze the data contained on the images. For example, the GIS operator will tell the computer what a deforested area looks like in the rainforest (by pointing the computer to a known deforested area), and the computer determines all other areas that resemble the type area (by comparing pixel values). The computer calculates the linear extent of features such as roads, pipelines, and rivers, and the areal extent of areas of interest such as cleared/deforested areas, oil spills, pits, and ponds. Much of the art of damage assessment using remote sensing lies in the GIS operator's ability to use various routines to analyze the raw data. Some of the GIS routines that we commonly use include contrast balancing and stretching, supervised classifications (maximum likelihood and others), unsupervised classifications (K means and others), principal components analysis, transformed vegetation indexing, and normalized differences.

Satellite Imagery: The resolution (i.e. size of each pixel) of satellite images currently varies from 10 meters (SPOT data) to 30 meters (Landsat Thematic Mapper data). Because of this resolution, satellite imagery is used as a basemap when large areas or features are being investigated, such as whole lease blocks or fields with hundreds of wells. Common examples include deforestation in the rainforest or roads built on permafrost. Multi-spectral data, such as that available from Landsat, is particularly useful for working with vegetation. By analyzing combinations of spectral bands, different features are highlighted (e.g. vegetation types, dead vegetation, surface water, bare earth). For example, many of the bands can be used in detecting vegetation types: bands 1-3 represent the visible spectrum; band 4 contains infrared spectra, and is useful for determining vegetation by approximating peak chlorophyll output; and bands 5-7 contain mid-infrared spectra approximating plant moisture content.

WALSH purchases satellite imagery in digital format, georeferenced (when possible). We use Landsat Thematic Mapper most often in vegetated areas, such as the Amazon rainforest, because the seven spectral bands can be used singly or in combination to accurately determine features such as cleared land and roads, and to discriminate between types of vegetation and landforms. We utilize SPOT satellite images in desert environments, or where greater resolution is needed. SPOT images are panchromatic (i.e. aren't divisible into spectral bands), but their 10-meter resolution provides significantly more detail. Other satellite image sources are available, and more will be available in the near future, including images from Russian satellites and from various private

consortia that are launching satellites.

Aerial Photographic Imagery: Aerial photography is used when a higher resolution is needed; for example when looking at individual production facilities such as tank batteries, compressor stations, well pads, and camps. WALSH utilizes aerial photographs from two sources: our own camera system, and commercial aerial photography services.

A complete camera system includes a helicopter mount, an autofocus 35mm camera with a data back, a video camera with digital image stabilization, a GPS unit, and a palmtop computer. The palmtop computer records times and locations from the GPS, which are correlated to the time stamp on the 35mm and video cameras. In this way, WALSH knows the exact geographic location of each photograph. The 35mm images are processed and digitized onto a Kodak CD. This allows importation directly into the GIS, while the GPS data attached to each image allow easy georeferencing with other images. Video images are taken along pipelines, seismic corridors, and roads, and are imported into the GIS using a digital image capturing device.

Mosaicked aerial photographs are excellent basemaps for field activities such as auditing, sampling, and reclamation planning and operations.

Global Positioning Systems (GPS): Often, remote sensing is used in conjunction with field activities such as sampling and audits. When conducting fieldwork, we use a GPS unit to quickly determine the location of sample points, wells, road intersections, and facilities. With the GPS, these locations are easily correlated with the base maps/images. GPS units with recording functions can also be used to determine the geographic boundaries of features such as lakes, tailings piles, eroded areas, and property lines. This is accomplished by walking the perimeter of a feature while recording with the GPS. The resulting data are easily converted by the GIS to an outline and the area quickly calculated.

The GPS is also used to georeference aerial photography, by warping the image so that known points on the image (corners of buildings, road intersections, etc.) correlate with their locations as determined by the GPS.

CASE STUDY: REMOTE AREAS - QUANTIFYING HISTORICAL DEFORESTATION OF A RAINFOREST

Problem: One of the major environmental impacts of exploration and production activities in rainforests is deforestation by colonists for small-scale slash-and-burn agriculture. A WALSH client is conducting exploration and production activities in a lease block in the Amazon Basin. There are many activities in their block, including their exploration and production, seismic projects conducted prior to their lease, large-scale commercial agriculture, a

pipeline and roads that traverse the block, and small-scale agriculture by colonists. Many of the environmental impacts in their block aren't related to the company's activities.

To facilitate their negotiations with the government, the company had two needs: 1) Determine how much deforestation had existed when they took over the block in 1985 (they hadn't determined baseline environmental conditions at that time), and 2) Determine how much of the deforestation that has occurred since 1985 is due to their activities, and how much is due to other factors.

Solution: WALSH acquired a Landsat Thematic Mapper image of the study area from 1985, and acquired a copy of a 1995 Landsat image already in the company's possession. The two images were imported into a GIS and geo-rectified. WALSH acquired CAD maps of oilfield facilities, seismic lines, and other features from the client, and imported it into the GIS.

Working with the client, we determined known areas of deforestation, and used these as "training sets" for supervised classification of the images by the GIS. In other words, we told the computer what deforestation looked like (pixel values and groupings, etc.), and used the computer to find all similar areas on the two images.

To accomplish the client's first goal (determining existing deforestation in 1985), WALSH ran supervised classification on the 1985 Landsat image. The result was a map of deforested areas that clustered along roads, pipelines, seismic lines, and rivers, all of which are used for access to the normally impenetrable rainforest. The GIS calculated the amount of deforestation in hectares. WALSH assigned a "buffer" zone around each feature (for instance, a 1000 meter buffer along roads, 500 meters along seismic lines, etc.). The GIS then grouped all deforested areas into categories according to what they were adjacent to. The result was a table that showed the amount of deforestation present that was due to each "factor." A portion of the table is reproduced as Table 2 (the data are confidential, so only the labels are shown).

The results from this table have been used by the client to show the government that a substantial amount of deforestation had occurred in the block prior to their lease.

To accomplish the client's second goal (determining deforestation and causes during their tenure in the block), WALSH ran similar supervised classification routines on the recent image. Deforested areas on the 1995 image that were virgin jungle in the 1985 image were categorized as having been impacted during the client's lease period. In addition, some of the previously deforested areas remained deforested, and some had begun to regrow (slash-and-burn agriculture abandons old fields once soil nutrients are depleted -- generally in several years' time. These areas then begin to regrow natural vegetation). A map was made showing recently deforested areas, previously existing deforested

areas that remained deforested, and areas undergoing regrowth. WALSH calculated the hectares of each type, and grouped them according to influence. By separating out features that are related to the company's activities (work camps, access roads, drill pads, seismic lines, pipelines, etc.) from features not related to their activities (commercial agriculture, other roads and pipelines, previously existing seismic lines, etc.), WALSH determined the percentage of the deforestation that has occurred during the client's lease is due to their activities. This has also proven useful in negotiations with the government.

CASE STUDY: LARGE PRODUCING FIELD - ENVIRONMENTAL AUDIT

Problem: A WALSH client was considering bidding on a lease block in South America with over 1,000 operating and abandoned wells. The field has been producing hydrocarbons for over 80 years. With little available time, the client needed to know the extent of existing environmental damage for factoring into their bid.

Solution: WALSH conducted an environmental audit consisting of three tasks: remote sensing and field reconnaissance, field investigation, and calculation of the extent of impacts. Because time was critical, we studied a representative portion of the block in detail and extrapolated these results to the rest of the block using satellite and aerial photo imagery.

Remote Sensing and Field Reconnaissance: A brief field reconnaissance identified a representative area with extensive visible contamination. WALSH first conducted an aerial video and photographic survey of this area. This area included surface oil spills at tank batteries and production facilities and areas damaged by produced water discharge. The survey was flown by helicopter. A video camera was run continuously throughout the flight and was linked to a television for in-flight viewing of the ground surface. High resolution 35mm still images were also taken. Selected images of contaminated sites were digitized and fed into WALSH's image processing system.

Field Investigation of Soil and Water: Next, WALSH conducted a field investigation of 24 representative contaminated sites including wells, manifolds, and tank batteries. Hard copies of the aerial images were used as base maps for plotting the extent of contamination.

Digital 35mm images (developed onto Kodak CD-ROM) and mosaicked video images were imported into a GIS. Final cell size and ground resolution of the imported images ranged from 8 inches to 2 feet. Prototype points (learning sets) were selected in areas that showed visible signs of surface contamination. After a range of values of contaminated soils were identified, the computer identified all other pixels that had the same spectral signature as the prototype

points. The total contaminated surface area of each facility was calculated and exported to a master database. The computer then generated an outline of the contamination which was checked against the original imagery for accuracy. The result of this step was a set of images in the area investigated in the field, with computer-drawn boundaries of surface oil spills.

Now that WALSH knew what oil spills looked like in digital imagery, the next step was to extrapolate this information on a regional basis using a SPOT satellite image. We compared the surface oil spills as determined on the ground and using 35mm/video imagery with the same sites as shown on the SPOT image. The oil spills were apparent on the SPOT image, and correlated well with the field investigation. We then had the GIS determine all other locations on the SPOT image that had the same pixel values as the known contaminated areas, and were adjacent to wellheads or other facilities (tank batteries, etc.). The result was an image showing about 500,000 square meters of probable surface oil contamination throughout the 1000-well field.

To assess the overall reliability of this detection technique, areas of contamination calculated from the SPOT image were statistically correlated with contamination estimates form the 35mm/video mapping. The correlation coefficient between SPOT and video/photo-CD was 0.90 for 16 facilities of interest. It was considered to be a reliable, conservative estimator for areal extent of surface contamination.

Calculation of the Extent of Impacts: WALSH then combined the areal extent of surface contamination as determined by the GIS and SPOT image with the known average depth of contamination determined during the field visit. Using these data, we estimated the volume of hydrocarbon contaminated soils to be about 1 million cubic meters. The client then used this volume to calculate the potential cost of remediation using industry-standard remediation costs.

CASE STUDY: HISTORICAL PERSPECTIVE - LOCATING FACILITIES THAT NO LONGER EXIST

Problem: A company needed to purchase a portion of property for a transportation corridor. A previous site owner had processed railroad ties, storing spent creosote and other wastes in an unlined pit. The pit had been removed in the 1950's, and no remains were visible. The company wanted to avoid purchasing the portion of the property that had formerly contained the pit, and had no way of knowing exactly where it had been.

Solution: WALSH located current and historic aerial photographs. The aerial photographs were scanned and imported into a GIS. Also imported into the GIS was the CAD map of the planned construction. Several buildings were found that existed in both aerial photographs, and these buildings were used to rectify

(georeference) the two photographs and engineering drawings.

The task was fairly simple. The outline of the pit was traced in the GIS and transferred to the recent aerial photograph and engineering drawing. This allowed accurate determination of the former areal extent of the pit. Unfortunately, the pit had existed in the area of the proposed construction, so the company had to modify the construction plans. However, by doing so, they were able to acquire land without acquiring the environmental liability associated with the former pit.

CONCLUSIONS

The use of remote sensing for environmental assessment involves GIS and GPS systems that are widely available. Common data sources used in oilfield damage assessment using remote sensing include satellite images; aerial photographs; CAD maps of seismic lines, facilities, and/or lease boundaries; and topographic or other base maps. Most of these data are available from commercial sources, or in-house within oil companies. The "art" of remote sensing lies in the specialized application of calculations and GIS routines to varying environmental settings and conditions. Here, a significant amount of experience is often required for remote sensing to be successful.

While remote sensing is not a substitute for ground-based observation of environmental damage in oil E&P areas, it provides a useful tool when ground-based observation is impractical or expensive, when large areas need to be viewed, or when a historical perspective is desired. An additional benefit of remote sensing is that it provides maps or images of environmental conditions that are easily understood and visually interesting.

Table 1
Common Sources of Environmental Impacts at Operating Oil Fields

Source	Location	Primary Impacts	Associated Secondary Impacts
Terrestrial oil spills	Batteries, flowlines, pipelines, tanks, gas plants	Soil contamination	Horizontal and vertical contaminant migration in surface and ground water
Produced water discharge to surface drainages	Production facilities, drilling pads	Soil and surface water contamination	Ground-water contamination
Oil spills on surface water	Oil-water separator pits	Surface water contamination	Surface water contamination, ground-water contamination, aquatic biota impacts, terrestrial biota impacts
Vegetation and soil removal and destruction from clearing operations	Roads, pipelines, flowlines, drill pads, camps	Vegetation and soil impacts	Erosion of topsoils, sedimentation of tributary streams and rivers, loss of habitat
Cut and fill slopes	Camps, facilities, drill pads	Topographic impacts	Disruption of surface drainages, flooding where roads cross drainages
Waste disposal	Drill pads, camps	Soil contamination	Ground-water contamination
Drilling mud pits, improperly abandoned oil-water separator pits	Drill pads	Soil contamination	Ground-water contamination

Table 2

Table Headings from Deforestation Table

Total Deforestation		By Responsible Party						By Time			
Factor	Total deforestation (hectares)	Directly related to oil company activities (hectares)	(%)	Indirectly related to oil company activities (hectares)	(%)	Due to other, none-oil company activities (hectares)	(%)	Deforestation Before 1986 (hectares)	(%)	Deforestation after 1986 (hectares)	(%)
Seismic lines	Confidential Data	Confidential Data						Confidential Data			
River											
Road											
Village											
Well pad											
Commercial Agriculture											

Financial Impacts of Legal and Regulatory Developments

Can Nonhazardous Oil Field Wastes Be Disposed of in Salt Caverns?[1]

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ABSTRACT

Solution-mined salt caverns have been used for many years for storing hydrocarbon products. This paper summarizes an Argonne National Laboratory report that reviews the legality, technical suitability, and feasibility of disposing of nonhazardous oil and gas exploration and production wastes in salt caverns (1). An analysis of regulations indicated that there are no outright regulatory prohibitions on cavern disposal of oil field wastes at either the federal level or in the 11 oil-producing states that were studied. There is no actual field experience on the long-term impacts that might arise following closure of waste disposal caverns. Although research has found that pressures will build up in a closed cavern, none has specifically addressed caverns filled with oil field wastes. More field research on pressure build up in closed caverns is needed. On the basis of preliminary investigations, we believe that disposal of oil field wastes in salt caverns is legal and feasible. The technical suitability of the practice depends on whether the caverns are well-sited and well-designed, carefully operated, properly closed, and routinely monitored.

INTRODUCTION

This paper provides a summary of a study recently completed by Argonne National Laboratory on the legality, technical suitability, and feasibility of disposing of nonhazardous oil and gas exploration and production wastes (referred to hereinafter as oil field wastes) in salt caverns (1). The author of this paper served as project manager for the study and was assisted by Deborah Elcock, Mary Raivel, Dan Caudle, Robert Ayers, Jr., and Ben Grunewald.

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U.S. SALT DEPOSITS

There are two types of subsurface salt deposits in the United States: salt domes and bedded salt. Figure 1 shows the location of U.S. salt deposits. Salt domes are large, generally homogeneous formations of salt that are formed when a column of salt migrates upward from a deep salt bed, passing through the overlying sediments. Salt dome deposits are found in the Gulf Coast region of Texas, Louisiana, Mississippi, and Alabama.

Bedded salt formations occur in layers bounded on the top and bottom by impermeable formations and interspersed with nonsalt sedimentary materials having varying levels of impermeability, such as anhydrite, shale, and dolomite. Unlike salt domes, bedded salt deposits are tabular deposits of sodium chloride that can contain significant quantities of impurities. Major bedded salt deposits occur in several parts of the United States. There are 16 states in which salt occurs in sufficient quantity to be mined by either excavation or solution mining or recovered through solar evaporation.

SALT CAVERN FORMATION

Salt caverns are formed by injecting water that is not fully salt-saturated into a salt formation and withdrawing the resulting brine solution. Figures 2 and 3 show the main features of salt cavern construction for caverns in domal salt and bedded salt, respectively. These figures are not drawn to scale or intended to show detailed construction features.

The petroleum industry has constructed many salt caverns for storing hydrocarbons. In an attempt to provide guidance for designing and operating hydrocarbon storage salt caverns, several organizations have developed standards and guidance documents (2), (3), (4).

USE OF SALT CAVERNS

The most common use of salt caverns is production of salt, which, in turn, enlarges the caverns. The postmining uses of caverns are hydrocarbon storage, compressed air storage, and waste disposal.

The earliest storage of hydrocarbons in bedded salt caverns occurred in the 1940s, with storage in salt dome caverns beginning in 1951. Some of the products that have been stored are propane, butane, ethane, ethylene, fuel oil, gasoline, natural gas, and crude oil. In 1975, the U.S. Congress created the Strategic Petroleum Reserve (SPR) program to provide the country with sufficient petroleum reserves to reduce the impacts of future oil supply interruptions. The SPR consists of 62 leached caverns in domal salt with a total capacity of 680 million barrels.

In the United States, waste disposal in salt caverns has been limited. In Texas, the Railroad Commission of Texas (TRC) issued six permits between 1991 and 1994 for disposing of nonhazardous oil field waste in salt caverns. The U.S. salt mining industry disposes of impurities removed during the brine purification process in caverns. Limited cavern disposal of wastes is occurring in Canada, Mexico, the United Kingdom, Germany, and the Netherlands.

REGULATORY CONSIDERATIONS

On July 6, 1988, the U.S. Environmental Protection Agency (EPA) published a list of those oil field wastes that were exempt from regulation as hazardous wastes under Subtitle C of the Resource Conservation and Recovery Act (RCRA) (53 FR 25477). On March 22, 1993, EPA issued clarification of the 1988 determination, adding that many other wastes that were uniquely associated with exploration and production operations were also exempted from RCRA Subtitle C requirements (58 FR 15284).

EPA's Underground Injection Control (UIC) regulations define Class II injection wells as wells that inject fluids that are brought to the surface in connection with natural gas storage operations or conventional oil or natural gas production. Most but not all of the wastes exempted by the 1988 RCRA regulatory determination would meet the UIC program's criterion to be "in connection with" oil and gas production. Some wastes (e.g., hydrocarbon-contaminated soil) would not meet the UIC criterion. Although the EPA's description of wastes that are "uniquely associated" with oil and gas production under RCRA cannot be clearly applied to determining whether such wastes have been brought to the surface "in connection with" oil and gas production under the UIC Class II regulations, the waste in question (i.e., the soil) has been contaminated by wastes that have been brought to the surface. Efforts are currently under way to obtain clarification from the EPA on whether all exempted oil field wastes can be injected into Class II wells.

At the state level, only the TRC has formally authorized disposal of oil field wastes into salt caverns. The TRC has issued permits for six facilities, but as of May 1996, only four of these were active. In April 1996, the TRC released draft proposed amendments to TRC Rule 9, the regulation that governs injection into a formation not productive of oil, gas, or geothermal resources. Ten other states were contacted about their interest in disposing of oil field waste in salt caverns. Many of these states were interested in following the TRC program to see how it worked, but at this time, only New Mexico has received an application for disposal of oil field wastes in salt caverns. There are no apparent regulatory barriers to the use of salt caverns for disposal of most types of oil field wastes at either the federal level or in the 11 states discussed in this analysis.

TYPES OF WASTES TO BE ACCEPTED

The types of oil field waste proposed for disposal in salt caverns are those that are most troublesome to dispose of through regular Class II injection wells

because they contain higher levels of solids. Wastes containing water that is not fully saturated with salt may increase the size of caverns because the unsaturated water will leach salt from the cavern walls. The presence of fresh water in wastes should not preclude their disposal in salt caverns, but the operator must account for the increased volume of the cavern and what effect it will have on such cavern siting parameters as distance to adjacent caverns and roof span or thickness. The solids-containing oil field wastes most likely to be disposed of in salt caverns include used drilling fluids, drill cuttings, completion and stimulation waste, produced sand, tank bottoms, and crude-oil- or salt-contaminated soil.

MONITORING AND RECORDKEEPING CONSIDERATIONS

It is in the best interest of both the regulator and the operator to know what types of wastes have been placed in the disposal cavern. The Interstate Oil and Gas Compact Commission (IOGCC) has published criteria that are intended to guide states in assessing and improving their regulatory programs for oil field waste management (5). While the IOGCC criteria do not specifically apply to disposal of oil field wastes by injection (which logically includes cavern disposal), they should be considered as a useful starting point for establishing monitoring requirements. It is appropriate to maintain long-term records of the source, quantity, and type of each batch of waste brought to the disposal facility.

CAVERN DESIGN AND LOCATION CONSIDERATIONS

Hundreds of salt caverns have been constructed and operated around the world. Most of these have been structurally sound and completely free from leakage or collapse. If cavern failure does occur, however, it can lead to contamination of surface water and groundwater. Caverns can fail through subsidence or collapse of the overlying material or through cracks resulting from increased pressures inside the cavern.

Reference (4) suggests several factors that should be considered for siting natural gas storage caverns. These factors are relevant for disposal caverns too.

- Distance to populated areas;
- Proximity to other industrial facilities;
- Current and future use of adjacent properties, including agriculture, which may withdraw large amounts of groundwater and potentially increase subsidence rates;
- Handling of brine or other displaced fluid;
- Proximity to environmentally sensitive wetlands, waters, and freshwater aquifers;
- Proximity to the salt boundary; and
- Proximity to other existing and abandoned subsurface activities (e.g., neighboring caverns for brine, gas, or hydrocarbons).

Another consideration for siting is the potential for seismic activity.

To minimize the chance for failure due to closure, collapse, or leakage, acceptable designs should be based on a geological review of the location that covers all features capable of affecting the cavern. Adequate studies should address regional stresses and strains; mechanical, chemical, and containment properties of the salt and confining rock formations; and structural anomalies, including faulting (4). The design should also consider potentially associated low-permeability zones and the effects of those zones on disposal operations (2). Detailed knowledge of the geology should be supported by adequate documentation. Operators should be able to demonstrate that the caverns they plan to use — either new caverns developed specifically for oil field waste disposal or existing caverns that are being converted — will remain stable in the future.

Following cavern construction and before waste disposal begins, inspection and testing should be conducted to verify the tightness of the cavern and to ensure that there is no hydraulic communication between the cavern and other caverns or elsewhere outside the salt formation.

During disposal operations, information on operation as well as measurements of subsidence and cavern integrity should be recorded periodically. Care must be taken to ensure against conditions that would cause the pressure at the cemented casing seat to exceed the fracture pressure. Emergency planning should also be undertaken to address accidental releases of brine or oily substances.

DISPOSAL OPERATIONS

Initially, caverns are filled with clean brine. Wastes are introduced as a slurry of waste and a carrier fluid (brine or freshwater). A carrier fluid that is not fully saturated with salt will eventually leach salt from the cavern walls or roof. Expansion of cavern diameter is generally not a problem as long as the anticipated degree of expansion is accounted for when designing the caverns. To avoid excessive leaching of the cavern roof, operators may intentionally introduce a hydrocarbon pad that, by virtue of its lower density, will float to the top of the cavern and keep the unsaturated carrier fluid from coming in contact with the cavern roof.

As the waste slurry is injected, the cavern acts as an oil/water/solids separator. The heavier solids fall to the bottom of the cavern, forming a pile. Any free oils or hydrocarbons that are associated with the waste float to the top of the cavern. Clean brine displaced by the incoming slurry is removed from the cavern and either sold as a product or disposed of in an injection well. When the cavern is filled, the operator removes the hydrocarbon pad and plugs the cavern. The remainder of this section provides greater detail on the disposal process and discusses issues related to disposal.

Fully saturated brine is a good carrier fluid, but it may not always be available or may be too costly. Using freshwater or brines that are not fully saturated as carrier fluids does not present major difficulties, however. Under this scenario, the operator would need to be aware of the effect the carrier fluids would have on additional salt leaching. Although the presence of freshwater should cause only a relatively small change in the diameter or height through leaching, under certain circumstances, the amount of additional leaching could reduce the intra-cavern distance, the distance to the edge of the salt formation, or the cavern roof thickness to a degree that would be considered undesirable.

There are three potential ways to fill the cavern:

1. The waste can be pumped down the tubing, and the displaced brine can be withdrawn from the annulus.

2. The waste can be pumped down the annulus, and the displaced brine can be withdrawn from the tubing.

3. The waste can be pumped down one well, and the displaced brine can be withdrawn through a second well.

The first scenario described above is the one most likely to be used. The heavier solids in the incoming waste will be introduced near the bottom of the cavern and will have a good chance of settling and remaining in the cavern. Some of the hydrocarbons rising through the cavern may become entrained in the displaced brine that is leaving the cavern, although most hydrocarbons will accumulate in a pad or layer near the roof.

As the solid components of the incoming waste fill the bottom of the cavern, an interface forms between the accumulated waste and the overlying brine, including a transition zone of brine that is mixed with the waste. Early in the life of a disposal cavern, brine is withdrawn hundreds of feet above the surface of the waste pile or the transition zone. The vast majority of the displaced brine will be clean. As the cavern fills, however, the transition zone brine may make up a larger proportion of the remaining cavern volume. At some later time, the brine withdrawn from the cavern will consist partially or completely of brine from the transition zone. The transition zone brine will be noticeably dirtier than the clean brine that was originally displaced from the cavern. The waste/brine interaction in the transition zone should have no effect on the nonhazardous classification of the brine or on the environmental suitability of cavern disposal. However, there may be unanticipated operational concerns and expenses.

Displaced brine is generally sold as a product or injected into brine disposal wells. As long as the brine is clean, either method of managing displaced brine can be practiced without additional treatment or handling. However, as the transition zone brine is displaced from the cavern, the operator may be faced with additional expense to clean up the brine before it can be

injected underground for disposal. Solids-laden brine could clog the formation into which it was injected; typically such wastes are filtered prior to injection. Since most of the brine that is sold is used as a constituent of drilling fluids to drill additional oil and gas wells, the presence of waste components in the brine may not affect its salability.

Monitoring of cavern pressure should be done before the cavern is filled with oil field waste, throughout the waste emplacement cycle, and, optimally, for some period of time after the cavern has been closed. To monitor cavern pressure after closure, a pressure transducer must be installed in the cavern at the time it is closed.

CLOSURE AND REMEDIATION

Although various industries have been operating storage and production caverns for years, the long-term behavior of caverns filled with oil field waste is unknown. Scientists have modeled cavern behavior, and engineers have conducted limited tests of closed brine-filled caverns. Most have studied liquid-filled salt caverns, although some have modeled hazardous waste disposal in dry caverns. The extent to which preliminary findings in these areas relate to the behavior of caverns used for oil-field wastes is not known. However, it will depend at least in part on the ratio of brine (or other liquid waste contents) to solids and on the densities of the solid wastes relative to those of the surrounding salt.

The general concern with sealing and abandoning a fluid-filled salt cavern is that the continued creep of the cavern can raise the fluid pressure at the top of the cavern to a value greater than that of the lithostatic pressure at that point. This condition can lead to a possible fracture in the area of the wellbore, allowing brine to be forced out of the cavern.

Space restrictions do not allow an in-depth discussion of the literature here. Readers are referred to the Argonne report (1) for more details. In one key study (6), the authors showed that the effect of geothermal heating, combined with the pressure from the creep of the salt formation, can cause internal cavern pressure to exceed lithostatic pressure within only two years. The authors conclude, however, that the predicted rate of brine pressurization is not high enough to result in fracturing of the salt.

A more recent study of the behavior of sealed solution-mined caverns suggests that the factors affecting cavern closure include not only brine heating and cavern creep but also rock salt permeability (7). More importantly, rock salt permeability, even if very small, allows some pressure release and leads to a final equilibrium pressure that can be substantially lower than the lithostatic pressure.

The Argonne report (1) provides a distillation of interviews with several experts in the cavern field on their opinions on long-term cavern stability. In summary, disposal of solids in brine-filled caverns will generally tend to enhance the stability of caverns. The degree of stability enhancement depends on the nature of the material. The interviewed experts generally believe that solids-filled caverns are unlikely to leak.

CONCLUSIONS

- This particular mode of disposal is in its infancy.

- There are no apparent regulatory barriers to the use of salt caverns for disposal of oil field wastes at either the federal level or in the 11 states discussed in this analysis. One area that would benefit from clarification is further EPA guidance on what types of wastes may be disposed of in Class II wells.

- The types of oil field wastes that are exempted from RCRA hazardous waste requirements are generally suitable for disposal in salt caverns. Many of these wastes are now disposed of in landfills or are land-farmed; these disposal methods pose environmental risks of their own.

- There are many variables to consider when siting, constructing, and operating a waste disposal cavern. The hydrocarbon storage industry has developed useful, detailed standards, guidance, and criteria for designing and constructing caverns; these are appropriate for waste disposal caverns, too. Hundreds of storage caverns have successfully been operated worldwide for several decades.

- There is no actual field experience on the long-term impacts that might arise from salt cavern storage of oil field wastes. The literature contains many theoretical studies that estimate what might happen following closure of a cavern. Although different authors agree that pressures will build in a closed cavern because of salt creep and geothermal heating, they do not specifically address caverns filled with oil field wastes. More field research and pilot studies on the effects of pressure buildup in closed caverns would aid our understanding of this subject.

- On the basis of this preliminary research, we believe that disposal of oil field wastes in salt caverns is feasible and legal. If caverns are well-sited and designed, operated carefully, closed properly, and monitored routinely, they represent a suitable means of disposing of oil field wastes.

REFERENCES

1. Veil, J.A., et al., "Preliminary Technical and Legal Evaluation of Disposing of Nonhazardous Oil Field Waste into Salt Caverns," prepared by Argonne National Laboratory, Washington, DC, for U.S. Department of Energy, June 1996.

2. CSA, "Storage of Hydrocarbons in Underground Formations - Oil and Gas Industry Systems and Materials," CSA Standard Z341-93, Canadian Standards Association, Rexdale, Ontario, Canada, July 1993.

3. API, "Design of Solution-Mined Underground Storage Practices," API Recommended Practice 1114, American Petroleum Institute, Washington, DC, June 1994.

4. IOGCC, "Natural Gas Storage in Salt Caverns - A Guide for State Regulators," Interstate Oil and Gas Compact Commission, Oklahoma City, OK, October 1995.

5. IOGCC, "IOGCC Environmental Guidelines for State Oil & Gas Regulatory Programs," Interstate Oil and Gas Compact Commission, Oklahoma City, OK, May 1994.

6. Ehgartner, B.L., and J.K. Linn, "Mechanical Behavior of Sealed SPR Caverns," paper presented at Solution Mining Research Institute's spring meeting, Houston, TX, April 25-27, 1994.

7. Berest, P., and B. Brouard, "Behavior of Sealed Solution-Mined Caverns," paper presented at Solution Mining Research Institute's spring meeting, New Orleans, LA, April 30-May 3, 1995.

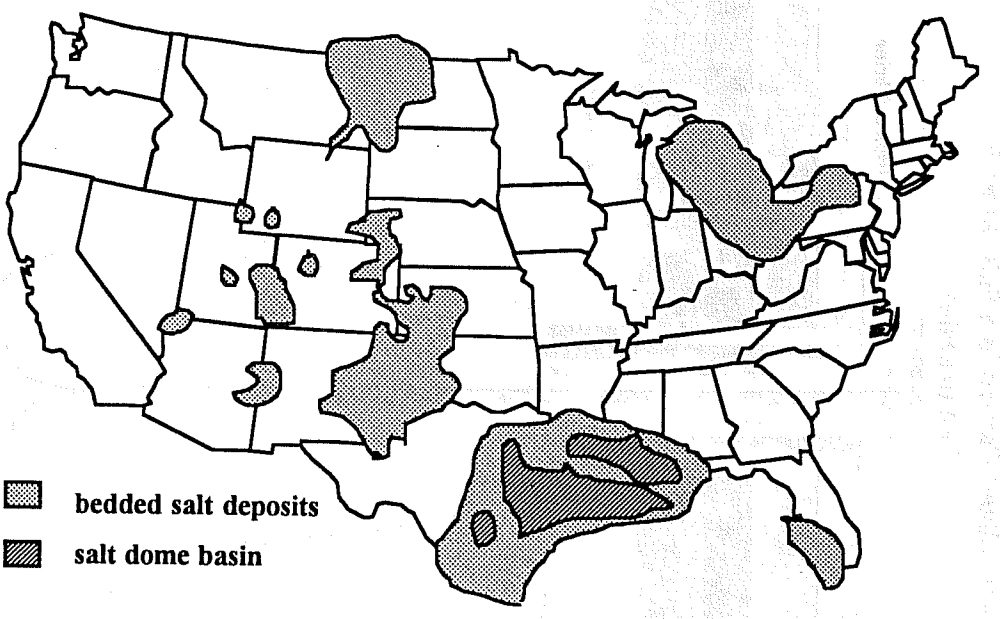


Figure 1 - Major U.S. Subsurface Salt Deposits

Figure 2 - Idealized Cavern in a Salt Dome Formation (not to scale)

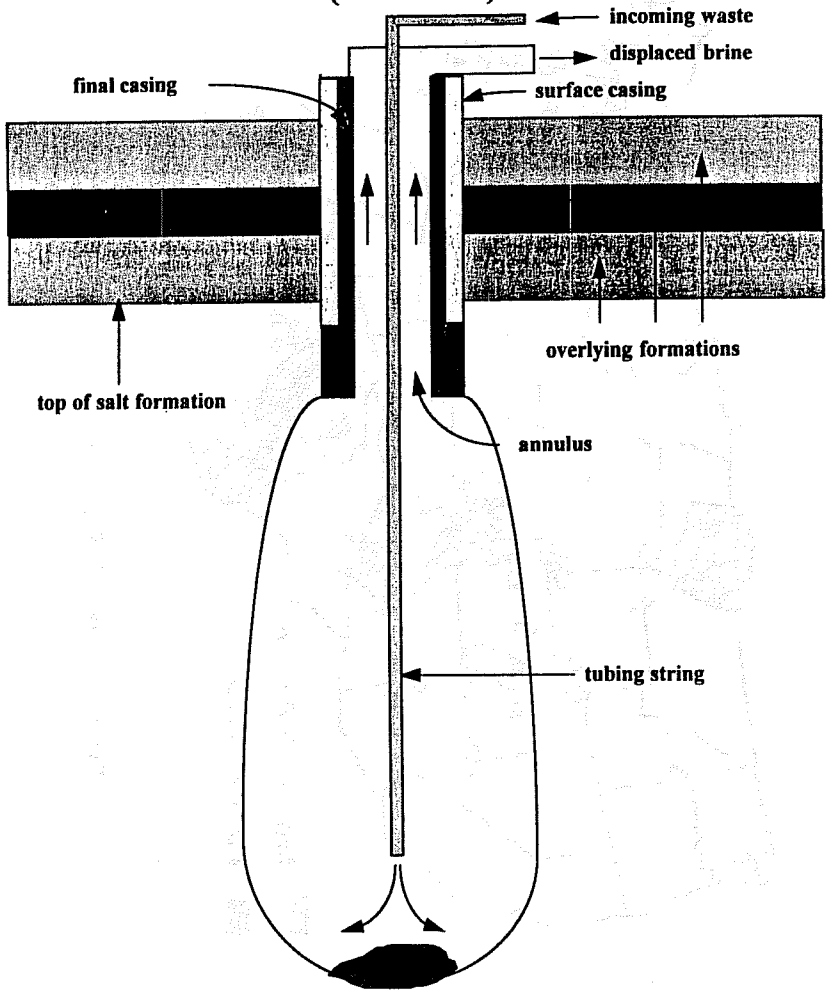
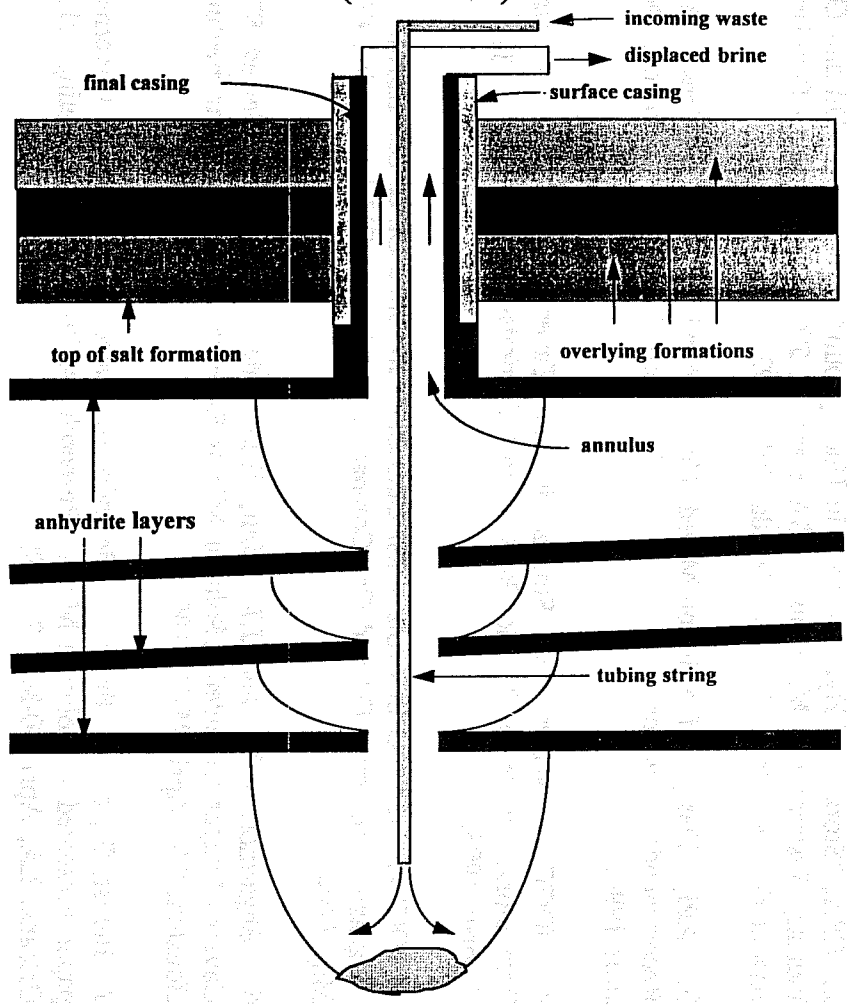


Figure 3 - Idealized Cavern in a Bedded Salt Formation (not to scale)



Oilfield Waste Management in Louisiana

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Abstract

Oilfield operators face significant challenges in dealing with cost-effective strategies regarding initial well location and drilling decisions, disposal of drilling and production wastes, proper permitting of pits, minimization of worker exposure to naturally occurring radioactive materials, and ensuring the proper closure of producing locations -- with the latter task often complicated by the divestiture of properties before production ceases. This presentation discusses such day-to-day problems faced by Louisiana operators and suggests practical ways of dealing with legal and regulatory environmental issues.

I. MANAGING OILFIELD WASTES

The management of oilfield wastes is affected by federal and state hazardous waste control laws, air control laws, water discharge control laws, nuclear radiation standards, and state conservation laws and regulations. In Louisiana, the two main regulatory agencies are the Department of Natural Resources, Office of Conservation, and the Department of Environmental Quality ("DEQ").

A. THE REGULATION OF "HAZARDOUS" AND "NON-HAZARDOUS" OILFIELD WASTES

As the reader is no doubt already aware, due to the exemption provided by the federal Resource Conservation and Recovery Act ("RCRA") most exploration

and production ("E&P") wastes are not regulated as "hazardous waste" under federal law. There is no specific exemption from Louisiana's Hazardous Waste Control Law for oilfield wastes. However, the term "hazardous waste" is applied "only to those wastes identified ... as such by the department, consistent with applicable federal laws and regulations." La. R.S. 30:2173(2). In addition, the DEQ's Hazardous Waste Regulations specifically exempt drilling fluids, produced waters, and other wastes associated with the exploration, development, or production of crude oil, natural gas or geothermal energy from regulation as hazardous wastes. LAC 33:V.105.D.14.

Other wastes not derived from oil and gas production or exploration are subject to RCRA permitting requirements, and standards for the treatment, storage, and disposal of such wastes. Operators should be careful to segregate and store such materials less than 90 days before shipment to a permitted hazardous waste disposal facility (storage beyond 90 days makes the facility a TSD facility subject to regulation as such, LAC 33:V.1109.E). Indeed, many materials found in the oilfield can be considered hazardous wastes when thrown away or discarded. Hydraulic fluids, crank-case oils, degreasing solvents, and other materials not used in actual exploration and production are common on many oilfield sites.

B. LOUISIANA'S CONSERVATION LAW GOVERNS THE ON-SITE AND OFF-SITE DISPOSAL OF NON-HAZARDOUS OILFIELD WASTE

The Louisiana Conservation Law, La. R.S. 30:4.C(1), 4:C(16)(a), authorizes the Commissioner of Conservation within the Department of Natural Resources to prevent the pollution of fresh water supplies by oil, gas, or salt water; to require the closure of pits, the removal of equipment, structures, and trash; and to otherwise require a general site clean-up of dry and abandoned wells.

1. STATEWIDE ORDER 29-B CONTAINS THE CORE REGULATIONS

Statewide Order 29-B, now codified as LAC 43:XIX.101, et seq. was first issued by the Commissioner in 1943. The rule has been greatly expanded (in the last decade especially) to regulate the handling of wastes generated in the exploration or production of oil and gas. While other state agencies are also involved in the regulatory process, Order 29-B establishes comprehensive treatment, storage, and disposal standards for oilfield wastes generated from drilling and production of oil and gas.

By statute, the person ordinarily responsible for compliance with 29-B and other orders of the Commissioner is the person who has the right to drill into and produce from a pool and appropriate production either for himself or others. La. R.S. 30:3(8). This in practice means the last operator of record for a well. Under certain circumstances, the Commissioner may look to past well operators, as necessary, to address waste problems. Recent amendments to the Louisiana Conservation Law, discussed in more detail in later sections of this paper, have also clarified this delineation of responsibility.

a. KEEPING TRACK OF THE DEFINITION OF NON- HAZARDOUS OILFIELD WASTES UNDER ORDER 29-B

The standards established in Statewide Order 29-B apply only to Non-Hazardous Oilfield Waste ("NOW"). NOW is defined as: "[W]aste generated by the drilling and production of oil and gas wells and which is not regulated by the provisions of the Louisiana Hazardous Waste Regulations." A detail listing of such wastes is provided in the rule.

Moreover, the Office of Conservation, Injection and Mining Division, has clarified that the another list of wastes otherwise associated with the oilfield do not meet the regulatory definition and may not be disposed of at permitted commercial oilfield waste disposal facilities. See Memorandum to Oilfield Service Companies, Commercial Oilfield Waste Disposal Facilities, and All Interested Parties, from James H. Welsh, Director, Injection and Mining Division, June 1, 1986.

b. OILFIELD WASTE TREATMENT AND DISPOSAL STANDARDS

For produced waters, Order 29-B requires disposal (1) onsite into subsurface formations not productive of hydrocarbons; or (2) onsite into man-made or natural drainage or directly into state waters provided such disposal conforms with any applicable state or federal discharge regulatory program (and, as discussed later, this method of disposal is being phased out by DEQ); (3) within the producing field into community disposal wells which operate without profit and for which all operating and maintenance costs are paid by owners of contributing wells (LAC 43:XIX.129.B.9.); or (4) by transportation offsite for injection into commercial disposal wells (Class II Wells). LAC 43:XIX.129.M. Note that generators (i.e., the well operators) of oilfield waste disposed of offsite

are expressly responsible for the proper handling and transportation of such waste. LAC 43:XIX.129.M.2.a.i.

For drill cuttings and drilling fluids, 29-B generally requires disposal (1) onsite through pit closure, land treatment, burial or trenching, or solidification, all of which are subject to specific technical limitations and requirements; or (2) disposal offsite by transportation, either through a transfer station or direct, to a commercial disposal facility. Any offsite disposal of either produced water or drilling cuttings and fluids, however, must be accompanied by a properly-completed manifest, a copy of which must be furnished to the Office of Conservation. LAC 43:XIX.129.M.6; LAC 43:XIX.129.B.7.

In addition to the above requirements, 29-B also authorizes disposal of reserve pit fluids and drill and workover waste fluids (1) into newly drilled wells which are to be abandoned or (2) into casing annulus of wells being drilled or wells which have been worked over, under stringent specifications and limitations. LAC 43:XIX.129.B.8.a.i.

c. STANDARDS FOR COMMERCIAL DISPOSAL FACILITIES LAC 43:XIX.129.M

A typical commercial disposal facility employs injection wells and land treatment as means of disposing of oilfield wastes. LAC 43:XIX.129.M.2.b. and M.7. However, as noted earlier, Statewide Order 29-B also envisions treatment that will provide for the reuse of waste materials, provided that certain testing criteria are met. LAC 43:XIX.129.M.8.

Before any material is off-loaded at a commercial facility, the shipment of NOW must be sampled and analyzed by facility personnel for pH, conductivity, and chloride content. Test records must be retained for at three years. LAC 43:XIX.129.M.5.i. Oilfield waste fluids may only be disposed of in what are termed Class II injection wells, which are wells authorized to receive such fluids. LAC 43:XVII.103.C.2. Further requirements for injection wells are found at LAC 43:XIX.129.H and additional requirements for commercial disposal facilities, including an increasingly rigorous permit process, are set forth at LAC 43:XIX.129.M.2.

Order 29-B has been strengthened in recent years to impose stricter financial responsibility requirements on commercial facilities, in order to ensure against any waste disposal incidents, and perhaps most importantly, to ensure that the site at the end of its life will be properly closed. As will be discussed later, many commercial operations (and many of which were operated prior to the

promulgation of any 29-B requirements) have closed, and their cleanup is the subject of ongoing regulatory concern.

d. OILFIELD PIT REQUIREMENTS

On January 20, 1986, Statewide Order 29-B was amended in order to require operators to notify the State of all existing pits by July 20, 1987. Any existing pit that was not to be utilized was to be closed by January 20, 1989. Moreover, an October 20, 1990 rulemaking amended Order 29-B in order to implement the provisions of Act 437 of 1989, which prohibited the construction, and ordered the phase out, of production pits in the coastal zone as of January 1, 1993.

Under the 1986 reporting program, the Office of Conservation received notification of 12,988 pits, although officials had estimated that there were approximately 20,000 pits throughout the state. Through mid-1991, industry had reported the closing of 8,507 pits.

For areas outside of the coastal zone, closed storage systems are encouraged, but not yet absolutely required. LAC 43:XIX.129.B.2.f. However, notification of any new pit (except for reserve pits which are handled as part of the well application) must be filed with the Office of Conservation at least ten days before construction. An Office of Conservation inspector must be given the opportunity to inspect the pit's construction. And, unless limited exemptions apply, oilfield waste storage pits permitted under existing law must have (1) a liner along the bottom and sides of the pit which has the equivalent of three continuous feet of recompacted or natural clay having a hydraulic conductivity no greater than 1 times 10^{-7} cm/sec; or (2) an alternate groundwater aquifer USDW protection system acceptable to the Office of Conservation. LAC 43:XIX.129.B.4.a.i(a) and (b).

e. OILFIELD WASTE CORRECTIVE ACTION STANDARDS

LAC 43:XIX.129B.4.f provides that if any continued operation of pits could result in the contamination of a groundwater aquifer, the discharge of fluids into state waters, or soil contamination outside the pit, any further use of the pit will be prohibited until all necessary corrective action is taken, including the possible institution of a groundwater monitoring program.

C. DISCHARGES OF OILFIELD WASTES INTO WATER

Oilfield exploration and production operations generate produced water, drilling muds, and other wastes which traditionally have been discharged into navigable waters. For years, such discharges have been subject to permitting requirements under both the Federal Clean Water Act, 33 U.S.C. §§ 1251-1376, and the Louisiana Water Control Law, La. R.S. 30:2071 et seq. In August 1996, however, the DEQ received final authority from EPA to administer the Clean Water Act's NPDES program.

The DEQ has established specific effluent standards for discharges associated with oil and gas exploration and production operations. LAC 33:IX.708. LWDPS permits based on these effluent standards contain effluent limitations governing the concentration and amount of pollutants that can be discharged. DEQ's effluent limitations are generally technology-based limitations established under the federal CWA, except in cases where the LDEQ determines that more stringent water quality based effluent limitations are necessary.

1. PRODUCED WATER

In 1991, DEQ completed a major rulemaking governing the discharge of waste oil, produced water, drilling fluids, drill cuttings, or other wastes or uncontrolled discharge of waste water. 17 La. Reg. 263 (March 20, 1991). The new rules imposed special restrictions on the discharge of produced water, depending on the area of the state in which it is discharged. First, operators with existing produced water discharges must have terminated such discharges into freshwater areas by July 1, 1992.

Second, for discharges into intermediate, brackish and saline water areas inland of the territorial seas, operators were required to submit a schedule by September 20, 1991 that would result in the phased elimination or compliance with the effluent limitations by January 1, 1995, unless the operator had only a single produced water discharge, in which case the schedule must achieve the limitations by January 1, 1994. An extension of time to comply with the effluent limitations would be considered "if submitted with the original compliance schedule," but no proposed extension would extend the date of discharge termination or effluent limitation compliance beyond January 1, 1997. LAC 33:IX.708.C.2.b.v.

Otherwise, produced water discharges into intermediate, brackish, and saline water areas inland of the territorial seas are now subject to effluent limitations for the following pollutants or pollutant properties: benzene, ethylbenzene, toluene, oil and grease, total organic carbon, pH, temperature, total

suspended solids, chlorides, dissolved oxygen, toxicity (acute and chronic), and soluble radium. No discharge carrying a visible sheen is allowed. Virtually all operators have ceased discharges rather than comply with these limitations.

Finally, produced water discharges into territorial seas have still allowed on a case-by-case basis, subject to exceptions.

2. DRILL CUTTINGS AND DRILLING FLUIDS

DEQ rules prohibit discharges of drill cuttings or drilling fluids, under the following conditions:

- no discharge of oil-based drilling fluids;
- no batch or bulk discharge of drilling fluids into water bodies inland of the territorial sea;
- no discharge of drilling fluids or drill cuttings within the boundaries of state or federal wildlife management areas, refuges, parks, or scenic streams or into any water body determined by the WPCD to be of special ecological significance;
- no discharge of drill cuttings or bulk drilling fluids within thirteen hundred feet (via water) of an active oyster lease, live natural oyster or other molluscan reef, designated oyster seed bed, or sea grass bed;
- in fresh and intermediate marsh areas, only discharges of drill cuttings generated onsite and their adhering native mud drilling fluids;
- no discharge of drill cuttings generated in association with the use of oil-based drilling fluids, inverse emulsion drilling fluids, or drilling fluids that contain diesel oil, waste engine oil, cooling oil, gear oil, or other oil-based lubricants; and

Documentation must be maintained detailing the nature and volume of all constituents added downhole in conjunction with drilling and workover operations. LAC 33:IX.708.C.3.

3. STORMWATER RUNOFF

The state's rules also prohibit stormwater discharges from any facility containing free oil or other oily materials as evidenced by a visible sheen or residual oil deposits or stains in the drainage area downstream of the discharge point. LAC 33:IX.708.C.4. The rule fixed stormwater runoff limitations for chemical oxygen demand, total organic carbon, oil and grease, and chloride.

4. DRILLING FLUID RESERVE PIT AND PRODUCTION PIT CLOSURES

DEQ rules prohibit the treatment and discharge of water from offsite oilfield waste disposal pits or pits containing waste other than non-hazardous oilfield waste. In addition, there are restrictions on the discharge of treated waste water from drilling site reserve pits, ring levee borrow ditches, shale barges, drilling fluid de-watering systems, and abandoned or inactive oilfield production pits that contain only non-hazardous oilfield wastes. Specific effluent limitations for water discharges from such pits include limitations on oil and grease, total suspended solids, chemical oxygen demand, chlorides, total chromium, and zinc.

Each discharge requires specific prior approval from the DEQ. To obtain such approval, an analysis of the treated waste water must be submitted to and approved by the DEQ prior to discharge.

D. NATURALLY OCCURRING RADIOACTIVE MATERIALS ("NORM")

Louisiana was the first state in the country to address issues relating to NORM associated with oilfield operations. The DEQ's Office of Air Quality and Nuclear Energy first issued NORM regulations effective February 20, 1989. LAC 33:XV.1401 et seq. These regulations provided for a general license to mine, extract, receive, possess, own, use, and process NORM without regard to quantity. The regulations also prohibited the transfer of land for unrestricted use if the levels of radium in soil were found above certain levels, and required general licensees to follow certain notification and site survey procedures.

Today, DEQ regulations establish a general licensing program for current operator sites where NORM has been detected either in equipment in levels exceeding 50 microrentogens per hour (including background) or in soils in levels exceeding 5 picocuries (pCi) per gram (above background). Owners of sites which

may contain NORM are required (and should have already performed) a "confirmatory survey" to determine NORM levels in soil or oilfield equipment, and to report "hot spots" to DEQ. Once a site is subject to the licensing program, worker protection requirements apply.

A NORM implementation manual, first prepared in conjunction with the 1992 rulemaking by DEQ and with input from the oil and gas industry, and now updated (albeit in draft form) to incorporate 1995 changes to the NORM rules, provides helpful guidance. In general, the manual tracts the regulatory requirements, and discusses exemption standards, instrumentation issues and procedures relating to the "confirmatory survey" of oilfield properties, general license requirements, treatment and disposal options, requirements for a release for unrestricted use, transportation and manifest rules, and the labeling and posting of equipment containing NORM.

With regard to NORM disposal, DEQ regulations now set forth the procedure that allows non-hazardous oilfield waste ("NOW"), containing NORM at concentrations not exceeding 30 pCi/gr, to be disposed of at 29-B commercial disposal facilities regulated by the DNR. (This authorization is contingent upon the subsequent treatment of the waste by dilution to levels of no more than 5 pCi/gr above background.) Moreover, specially-licensed NOW facilities may receive NORM waste that exceeds 30 pCi/gr but does not exceed 200 pCi/gr. A memorandum of understanding between DEQ and DNR guides this disposal process.

II. CLEANUP OF OILFIELD WASTE SITES

A. EPA'S MOVE TO ASSERT SUPERFUND JURISDICTION

In spite of RCRA's exemption of drilling wastes from the definition of hazardous waste (referenced, in turn, in CERCLA), the EPA placed on the Superfund National Priorities List three Louisiana sites which were used primarily for the disposal of "oilfield waste." These sites are all located near Abbeville, Louisiana, and include the D.L. Mud, Inc. site, the Gulf Coast Vacuum Services site, and the PAB Oil & Chemical Services site. EPA's position is that CERCLA grants the agency authority to consider oilfield wastes as containing CERCLA-regulated "hazardous substances." Two federal court decisions provide authority for this viewpoint. Eagle Pitcher Industries v. EPA, 759 F.2d 922 (D.C. Cir. 1985) (mining wastes deemed to contain CERCLA-regulated "hazardous substances," but these are now also managed as RCRA hazardous wastes); Louisiana-Pacific Corporation v. Asarco Inc., 1993 U.S. App. Lexis 24404 (September 23, 1993) (same; implicitly overruling U.S. v. Iron Mountain Mines,

Inc., 812 F. Supp. 1528 (E.D. Cal. 1992), which had specifically rejected Eagle-Pitcher rationale.)

B. LOUISIANA'S 1993 OILFIELD SITE RESTORATION ACT

This program is discussed in another paper being presented today, entitled "Recent Developments under Louisiana's Oilfield Site Restoration Law."

III. WETLANDS CONCERNS: DECIDING ON WHERE TO DRILL

In Louisiana, the ability to locate and drill oil and gas wells in a coastal area is governed in part by the Louisiana Coastal Zone Management Act, La. R.S. 49:213.1, et seq. Under this law, a coastal use permit is required for all activities having direct and significant impact on coastal waters. La. R.S. 49:214.23.(8). Mitigation is also required under La. R.S. 49:214.41. Importantly, the drilling permits issued by the Office of Conservation have been considered in lieu of coastal use permits provided such drilling permits are consistent with the Louisiana Coastal Zone Management Program. La. R.S. 49:214.31.B. However, Act 995 of 1991 provided that coastal use permit conditions supersede variances or exceptions granted by the Commissioner of Conservation for activities within the coastal zone.

Moreover, under the Clean Water Act, the U.S. Army Corps of Engineers ("COE") issues permits for the discharge of dredged or fill material into waters of the United States, which are broadly defined to include coastal and freshwater wetlands. 33 U.S.C. § 1344. The Corps also issues permits under Section 10 of the Rivers and Harbors Act, 33 U.S.C. § 403, which prohibits the creation of any obstruction to the navigable capacity of any waters of the United States without a COE permit.

Thus, to site an oil well in Louisiana's coastal zone in an area that is also considered a "wetland," both a federal Section 404 permit and a state coastal use permit (or drilling permit) are required. Both the COE and the state, however, have promulgated several general permits to facilitate this process; and, the dual permitting scheme has been designed to minimize duplicate filings.

Presentation of a Methodology for Area-of-Review (AOR) Variances and Description of Variance Studies Completed and in Progress

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Abstract

The Underground Injection Control (UIC) Regulations promulgated by the U.S. EPA in 1980, under the Safe Drinking Water Act of 1974, require Area-of-Review (AOR) studies be conducted as part of the permitting process for newly drilled or converted Class II (oilfield) injection wells.

A methodology for identifying areas that would be eligible for variance from AOR requirements has been developed at the University of Missouri-Rolla (UMR) under sponsorship of the American Petroleum Institute (API). The methodology provides for evaluation of an area for variance based upon five criteria. These criteria could be used in any order, singly or in combination, to exclude some or all wells from the AOR process. Wells not excluded by variance would be subject to well-by-well AORs.

The AOR variance methodology developed at UMR has been widely endorsed by the petroleum industry and state and federal agencies. As an example of endorsement, the Texas Railroad Commission (RRC) has authorized an AOR variance for the East Texas field and has subsequently proposed modification of its rules to include the opportunity for AOR variances on the basis of the UMR methodology.

Under sponsorship from API and the U.S. Department of Energy (DOE), AOR variance studies have been completed for the San Juan Basin of New Mexico, the Permian Basin of Texas and the East Texas field. A DOE sponsored variance study is in progress for The Texas Gulf Coast. Full-state preliminary variance studies, sponsored by API, are also being completed for California and Oklahoma.

Introduction

The Underground Injection Control (UIC) Regulations (1) promulgated by the U.S. EPA in 1980, under the Safe Drinking Water Act of 1974, require Area-of-Review (AOR) studies be conducted as part of the permitting process for newly drilled or converted Class II (oilfield) injection wells(2). Existing Class II injection wells operating at the time regulations became effective were excluded from the AOR requirements.

In January 1988, the EPA initiated a Mid-Course Evaluation (MCE) of the adequacy of its regulations for Class II injection wells. As a result of the MCE, EPA's Office of Drinking Water identified areas of concern to be further studied. Among the areas of concern was the need to further evaluate AOR requirements.

In April 1991, the agency formed a Federal Advisory Committee (FAC) to identify regulatory gaps and make recommendations for program changes. A March, 1992, Final Document summarized the FAC recommendations (See 3 or 4). The FAC Final Document recommends that an exception to this AOR requirement should be allowed in areas that have been granted a variance based upon criteria presented in an approved variance plan.

A methodology for identifying areas that would be eligible for variance from AOR requirements is documented in a final report from UMR(3) to the API and in an adaption of that report(4). That methodology is summarized below along with examples of its application to areas in New Mexico, Texas, California and Oklahoma.

Present Requirements for AOR Studies

DEFINITION OF THE AOR. An AOR is the area surrounding an injection well or wells defined by either the radial distance within which pressure in the injection zone may cause migration of the injection and/or formation fluid into an underground source of drinking

water (USDW) or defined by a fixed radius of not less than one-fourth mile.

INFORMATION REQUIRED FOR AN AOR. For an AOR study, in conjunction with an EPA UIC Class II injection well permit application, an applicant is required to submit a map showing all wells of any type within the AOR and a description of each wells type, construction, date drilled, location, depth, record of plugging and/or completion. Significant other geologic and engineering information is also required.

AOR Variance Methodology

The following discussion describes a methodology(3,4,5) developed for identifying a producing basin, trend, region or field or a portion of such areas which would be eligible for variance from AOR requirements. Five general methods (Fig. 1) are proposed for obtaining variance from well-by-well AORs. These methods can be used in any order, singly or in combination, to provide variance for some or all wells. Wells not excluded by variance would be subject to conventional AORs.

It is believed that all five of the methods can be applied over large geographic areas but the four methods based upon geologic and hydrologic criteria are most easily visualized as "global" methods. The fifth method requires evaluation of the manner by which the wells in the area under consideration were completed and abandoned.

VARIANCE BASED ON ABSENCE OF USDW. In some oil and gas producing areas, there are no USDWs. Any appropriate studies may be used to document this and to justify the granting of a variance from the AOR requirement.

Further, "exempted aquifers" by regulatory definition are not USDWs (6) even though ground water total dissolved solids are less than 10,000 mg/l. States have exempted numerous aquifers since inception of the UIC program. Other aquifers may meet the criteria exemption and operators may petition to have these aquifers exempted(7).

VARIANCE BASED ON LACK OF INTERSECTION. "No Intersection" refers to the situation where a USDW exists and overlies a zone with Class II injection operations, but none of the wells adjacent

to the injection well are drilled to a depth which penetrates the injection zone.

VARIANCE BASED ON NEGATIVE FLOW POTENTIAL. The FAC recommendations provide for the possibility of variance from the AOR process where the petroleum reservoir is underpressured relative to the USDW.

Flow potential information is generally available as measured water level (potentiometric head) data from wells completed in USDWs and as petroleum reservoir pressure data from oil and gas wells. References 3,4, and 8 provide detailed discussion of the procedures for conversion of petroleum reservoir pressure data to potentiometric head data for comparison with USDW potentiometric head data. The procedures call for subtraction of USDW heads from petroleum reservoir heads to obtain a residual value. Areas with negative residual heads would be ones in which a variance based upon lack of flow potential would be possible.

VARIANCE BASED ON MITIGATING GEOLOGICAL FACTORS. The FAC variance criteria include the availability of local geologic conditions that preclude upward fluid movement that could endanger USDWs. Such mitigating geological factors include sloughing, squeezing and sink zones.

A sloughing formation refers to any geological horizon which is highly incompetent and tends to fall or cave into the wellbore, bridge off, and form a solid barrier to flow. A squeezing formation is one with strata that flow plastically under the overburden stress to close an uncased borehole or to close the casing-formation annulus in a cased well. Examples of sloughing and squeezing formations include unconsolidated shales, consolidated bentonitic shales, salt and anhydrite.

A thief or sink zone refers to a geological horizon which has a flow potential less than the overlying USDWs and the petroleum reservoir which contains injection operations. Thief zones, as used here, are intermediate formations (located between an injection zone and a USDW) which act to divert the fluids flowing up the wellbore. A thief zone can also be a normally-pressured formation that is so permeable and thick that it diverts virtually all upward flowing fluid(9).

VARIANCE BASED ON WELL CONSTRUCTION AND ABANDONMENT METHODS. Well Construction and abandonment

methods can also be considered as a factor for an AOR variance. This is because the manner in which a well is constructed or abandoned may preclude fluid migration, even if a positive hydraulic flow potential does exist. States which have oil and gas production have historically set forth standards for well construction and abandonment. These standards detail the correct use or placement of casing, cement, bridge plugs, and other mechanical barriers in a wellbore.

Alternative Variance Approaches. On the basis of the historic sequence of development of construction and abandonment laws, regulations and practices, it is believed logical that well construction/abandonment based variances should be available through several different approaches, which are: 1. Field discovery and development occurs after promulgation of well construction and abandonment standards that provide adequate USDW protection. 2.Sufficient AORs exist and provide statistical evidence that all wells protect the USDWs. 3. A representative sample of wells is found to provide adequate protection to USDWs. Wells are evaluated with respect to flow barriers and plugs.

VARIANCE BASED ON OTHER COMPELLING EVIDENCE. While the authors and the many others that have participated in guiding and reviewing their work have attempted to identify as many bases for qualifying an area for variance as possible, there may be other opportunities that have been overlooked. In developing a variance plan, the states and EPA regions should remain flexible and not limit the information that will be considered in determining whether to grant a variance. This flexibility is needed to ensure variances can be obtained in all areas where injection wells pose sufficiently low risk to USDWs.

AOR Variance Studies Completed and in Progress

SAN JUAN BASIN OF NEW MEXICO. The first area to which UMR applied the AOR variance methodology described above was the San Juan Basin of New Mexico. The results of that study are described in a final report(10) to the API and in a summary paper(11).

The San Juan Basin is a nearly circular basin in the Four Corners region of New Mexico. Most of the basin is located in New Mexico, although the outer margins are located in Colorado, Utah and Arizona (Figure 2).

Oilfields with injection operations were identified and located throughout the basin. There were 24 oilfields with active injection operations in the San Juan Basin. No single variance criterion applied to all fields in the basin. There are, however, criteria that apply widely throughout the basin. These include: 1. Development of the field post-dates the establishment of regulations or rules that provide for adequate USDW protection. 2.Examination of a sample population of wells establishes that wells are constructed and abandoned so that they provide adequate USDW protection. 3. Sloughing and/or squeezing zones are present that may preclude upward fluid movement through an open wellbore or behind casing.

At least two variance criteria were found to apply to all 24 fields and are believed to provide good possibilities for variances for 20 fields, and some possibilities for the remaining four.

PERMIAN BASIN OF TEXAS. The AOR variance methodology has been applied to the Permian Basin, Texas, in order to determine the level of protection which producing and abandoned wells provide to USDWs throughout the basin(14).

The Permian Basin (Figure 3) refers to an area in West Texas and New Mexico that is one of the most prolific oil producing areas of the world. Figure 3 shows the eleven west Texas counties included in the UMR study and the location of major oilfields evaluated in the study. A statistically valid sample of producing wells and plugged and abandoned wells was studied in the 78 injection fields to determine the extent to which the construction and abandonment characteristics of these wells are protective of USDWs.

Examination of the well records for selected producing wells has shown that Permian Basin producing wells are constructed so that they are protective of USDWs.

With the exception of wells for which no records could be located, all abandoned wells examined in the Permian Basin study had plugging forms which showed notification to and approval by the RRC. Based on the examination of records of abandoned wells in the Permian Basin study, it was determined that wells abandoned during and after 1967 have adequate and appropriately placed cement plugs to provide USDW protection. All but a few pre-1967 wells examined had RRC plugging forms available. Examination of those abandonment records indicated that nearly all wells with records have adequate and

appropriately placed cement plugs and are protective of USDWs. A few did not have cement plugs; however, in those wells, casing, behind casing cement, mud laden fluid and other features provide USDW protection. Comparison of the wells without RRC plugging forms with other nearby wells showed that those few wells lacking abandonment records probably do provide USDW protection.

On the basis of the findings of this study, it is believed that the 78 injection fields should qualify for AOR variances based upon well construction and abandonment characteristics. By extension, other fields in these counties and in adjoining counties should also merit consideration for variances.

EAST TEXAS FIELD. The East Texas oil field is located in the extreme eastern part of Texas and comprises approximately 131,000 acres(Fig. 4). The field was discovered in 1930 and is the largest oil field in the conterminous United States in the number of wells and volume of oil produced (15).

Because of pressure declines in the reservoir, the field has been undergoing water injection for pressure maintenance since 1938(16). As of 1995, a total of 104 Class II salt-water disposal wells, operated by the East Texas Salt Water Disposal Company (SWDC), were returning all produced salt water to the Woodbine sand producing reservoir.

At the suggestion of various East Texas field operators, and with the agreement and encouragement of the SWDC and the RRC, UMR proposed to DOE a study of AOR variance opportunities for the East Texas field. A Steering Committee recommended that UMR study the variance method based upon the lack of sufficient petroleum reservoir pressure to cause flow into the lowermost USDW. A 1995 report documents the results of UMR's investigation of this variance option (17).

The general process for this study was: 1. Obtain reliable petroleum reservoir pressure data, ground water head elevations for the lowermost USDW and elevation data for the base of the lowermost USDW. 2.Convert reservoir pressure data to fresh-water head elevations using the base of the lowermost USDW as a datum. 3. Subtract USDW heads from petroleum reservoir fresh-water heads to obtain head residuals. Negative residuals reflect an underpressured petroleum reservoir.

Very good quality data were obtained for reservoir pressure, USDW heads, elevation of the base of the USDW and reservoir engineering properties. Using these data, maps were prepared and contoured that display the information necessary to compare fresh-water equivalent heads of the Woodbine reservoir with Carrizo-Wilcox USDW heads. The comparison process shows that Woodbine reservoir pressure would have to be increased by a minimum of 173 psi to balance the USDW heads and a pressure increase greater than 173 psi is needed to initiate upward flow of reservoir water into the USDW.

The UMR analysis showed that the Woodbine reservoir is currently underpressured relative to the Carrizo-Wilcox USDW and will remain so over the next 20 years. This information provides a logical basis for a variance for the field from performing AORs. Relief from the need to perform AORs would significantly benefit all field operators, but particularly smaller ones to whom incremental costs are most important. On August 25, 1995, the RRC formally approved a variance from AORs for the SWDC and other operators in the East Texas field, on the basis of the UMR report (17).

STUDIES IN PROGRESS

Texas Gulf Coast. Under sponsorship of the DOE, a study is currently underway of AOR variance opportunities in the Texas Gulf Coast petroleum producing province. This study was initiated in early 1995 and is scheduled for completion by May, 1997.

The study began with selected oilfields in Refugio County and has since expanded to include fields in eight other Gulf Coast counties. Class II injection wells in this area are brine disposal wells that usually inject into Miocene or Pliocene age sands that are shallower than the producing reservoirs but below the lowermost USDW.

The most promising AOR variance strategy appears to be a combination of compelling evidence based on well construction and abandonment plus mitigating geologic circumstances based on the sloughing and caving nature of the unconsolidated Miocene and Pliocene age shales that are present between the deepest USDW and the uppermost injection zone.

California and Oklahoma. Under sponsorship by API, preliminary studies are in progress of AOR variance opportunities in California and Oklahoma. These studies are intended to characterize the broad

petroleum geology and hydrogeology, regulatory framework and historic well construction and abandonment practices sufficiently to indicate the most promising AOR variance opportunities for each state. The studies are scheduled for completion during 1996.

Acknowledgements

Funding for the East Texas field study and the ongoing Texas Gulf Coast study is from the DOE under DOE Grant No. DE-FG22-94 MT94002. All other work described in this paper has been supported by the API. Acknowledgements to numerous individuals and groups are contained in the papers and reports for each of the separate studies that are briefly described here.

References

1. 40 CFR, Parts 144, 145 and 146.
2. 40 CFR, Part 146, Subpart C, 146, 24.
3. Warner, D.L., Koederitz, L.F., Dunn-Norman, S., and Laudon, R.C., "An Area of Review Variance Methodology," Final report from the University of Missouri-Rolla to the American Petroleum Institute, American Petroleum Institute, Washington, DC, 110 p., (1993).
4. "Technical Criteria for an Area-of-Review Variance Methodology," Underground Injection Practices Research Foundation, Ground Water Protection Council, Oklahoma City, Oklahoma, (Jan. 1994).
5. Warner, D.L., Koederitz, L.F., Dunn-Norman, S., and Laudon, R.C., An Area of Review Variance Methodology, SPE 28348, in Proceedings SPE Annual Technical Conference, Drilling and Petroleum Engineering, p. 499-506 (Sept. 1994).
6. 40 CFR, Part 146.3.
7. 40 CFR, Part 144.16.
8. Laudon, R.C., Warner, D.L., Koederitz, L.F., and Dunn-Norman, S., "Determination of Flow Potential from Oil Reservoirs to Underground Sources of Drinking Water in the San Juan Basin, New Mexico," Jour. Am. Assoc. of Petroleum Geol. Division of Environmental Geosciences (June, 1994) 1,1.
9. Warner, D.L., and McConnell, C.L., "Assessment of Environmental Implications of Abandoned Oil and Gas Wells," Journal Petroleum Technology, Vol. 45, No. 9 (Sept. 1993), p. 874-880.
10. Warner, D.L., Koederitz, L.F., Dunn-Norman, S., and Laudon, R.C., "Application of an Area of Review Variance Methodology

to the San Juan Basin of New Mexico," Final report from the University of Missouri-Rolla to the American Petroleum Institute, American Petroleum Institute, Washington, DC, 171 p., (Dec. 1995).

11. Dunn-Norman, S., Warner, D.L., Koederitz, L.F., and Laudon, R.C., Application of an Area of Review Variance Methodology to the San Juan Basin, New Mexico, Society of Petroleum Engineers, SPE Paper 29762, in SPE Advanced Tech. Series, V. 4, No. 2, (1996).
12. Kuhn, P.J., "Oil and Gas in the Four Corners:", National Petroleum Bibliography, Amarillo, 298 p., (1958).
13. Fassett, J.E., Thomaidis, N.D., Mathany, M.L., and Ullrich, R.A., ed.(1978, 1978, 1983), "Oil and Gas Fields of the Four Corners Area:", Four Corners Geological Society, Durango, Volumes I (1978) and III (1983), 1142 p.
14. Warner, D.L., Koederitz, L.F., Dunn-Norman, S. and Laudon, R.C., Application of an AOR Variance Methodology to the Permian Basin, Texas, Final report from the University of Missouri-Rolla to the American Petroleum Institute, Washington, D.C., 288 p. (March, 1996).
15. McWilliams, Jack, Large Saltwater-Disposal Systems at East Texas and Hastings Oil Fields, Texas in Underground Waste Management and Environmental Implications, T.D. Cook, ed., Am. Assoc. of Petroleum Geologists Memoir 18, p. 331-340 (1972).
16. East Texas Salt Water Disposal Company, Salt Water Disposal, East Texas Field, Second Edition, Petroleum Extension Service, University of Texas, 129 p. (1958).
17. Warner, D.L., Koederitz, L.F., Laudon, R.C. and Dunn-Norman, S., Evaluation of Area of Review Opportunities for the East Texas Field, Final Report to the U.S. Department of Energy on Phase I of U.S. DOE Grant DE-FG22-94MT94002, 89 p., (May 1995).

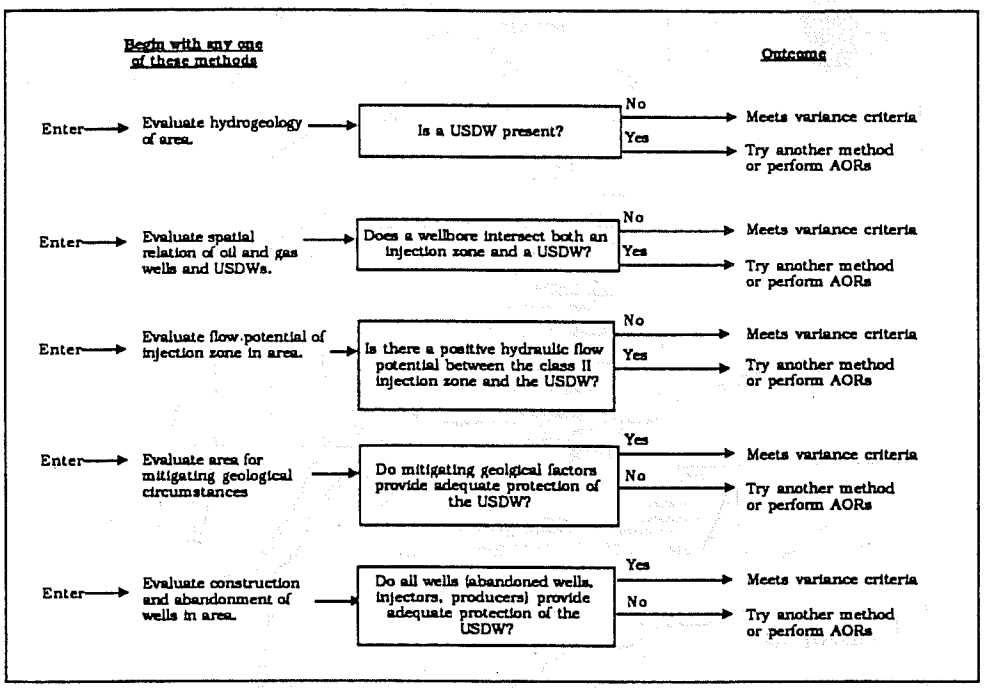
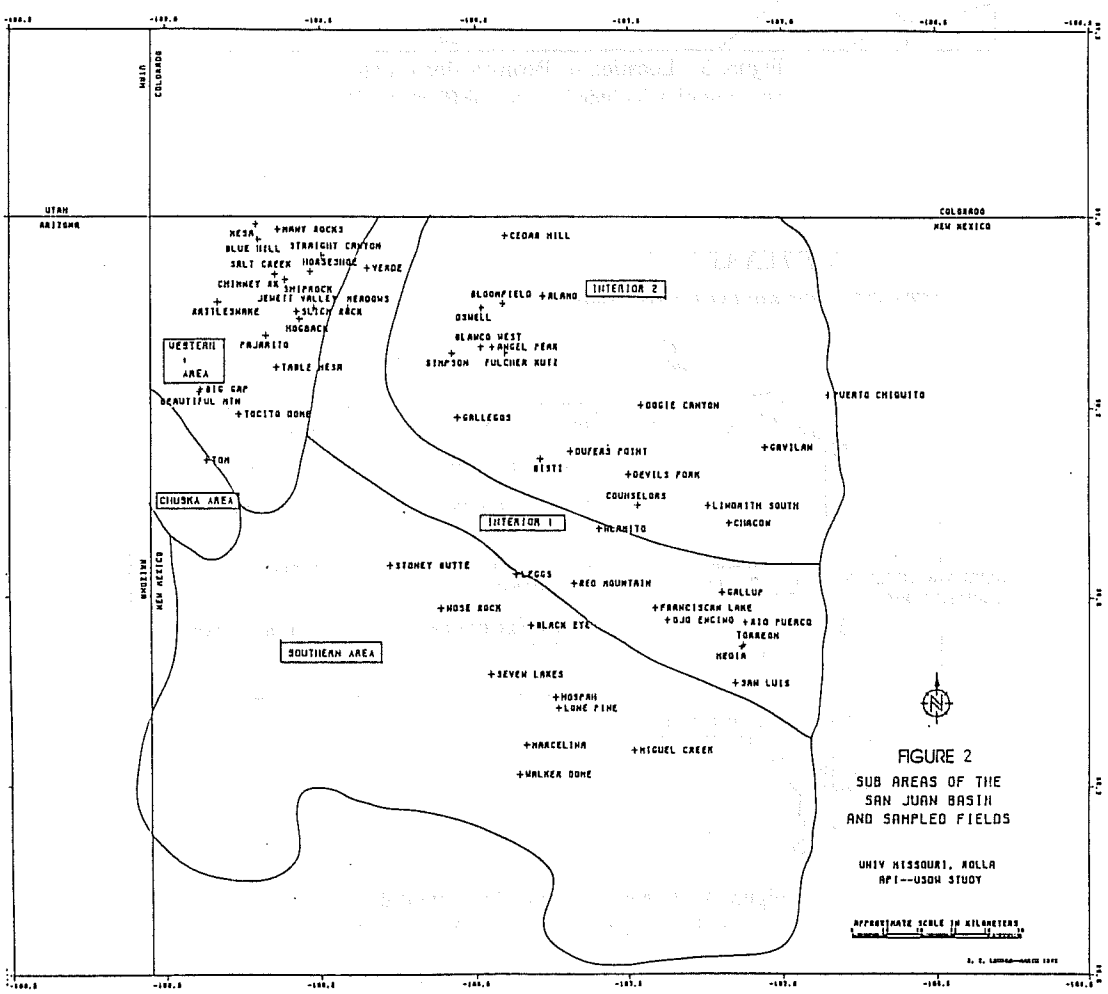


Figure 1. AOR Evaluation Methodology



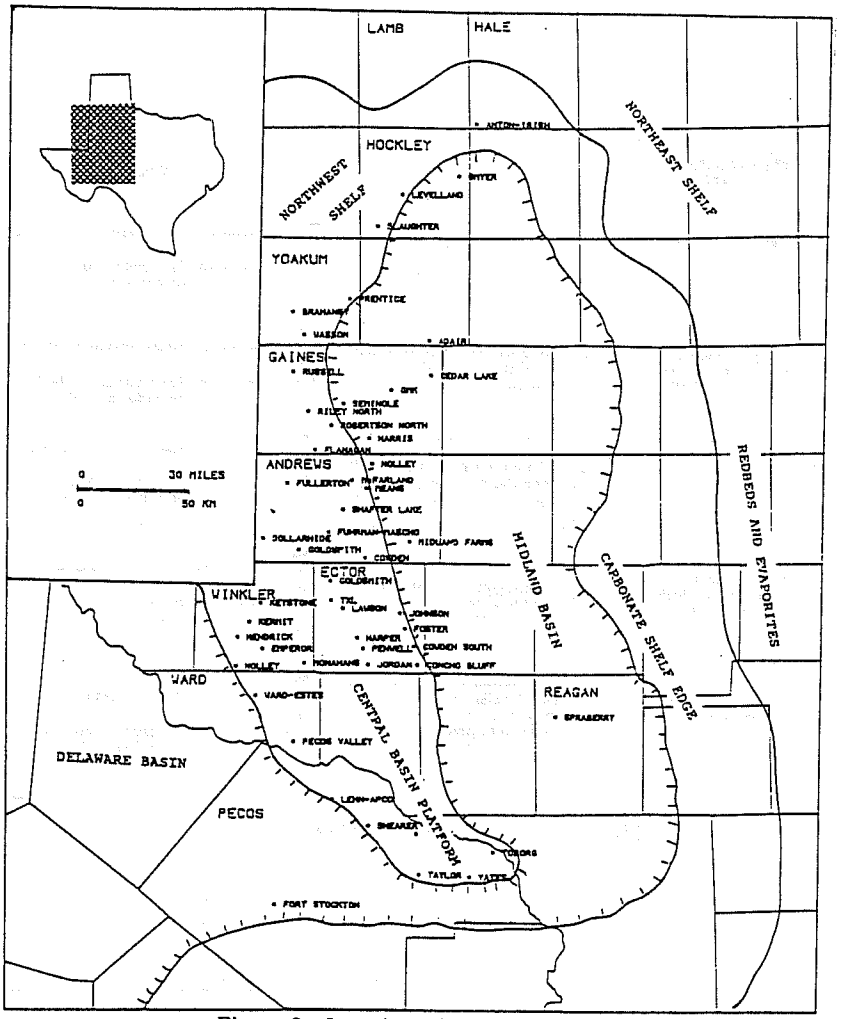


Figure 3. Location of Permian Basin fields and counties included in the UMR study (14).

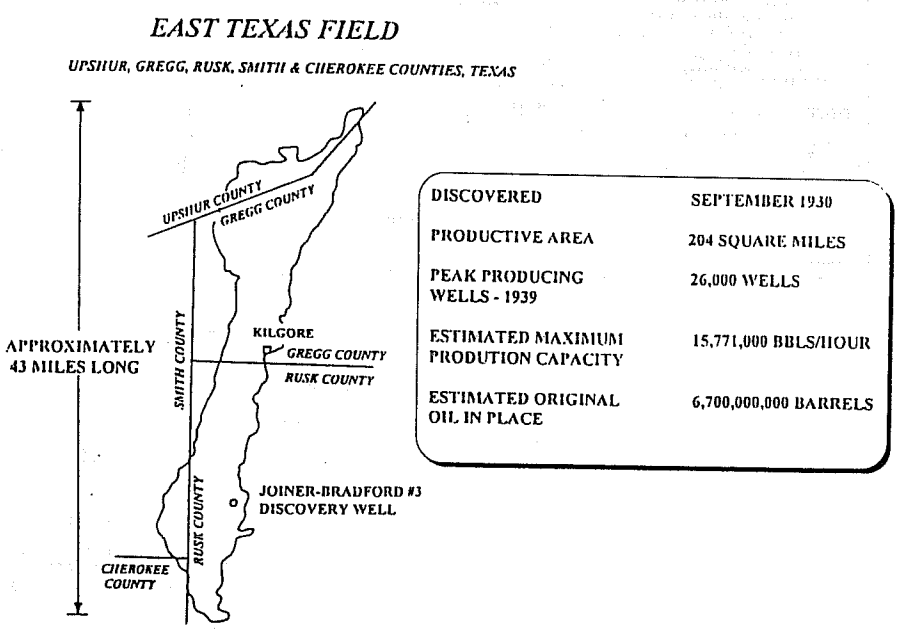


Figure 4. Location map and pertinent data for the East Texas field (Modified from 15).

Recent Developments Under Louisiana's Oilfield Site Restoration Law

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Abstract

This paper will report on recent developments under Louisiana's Oilfield Site Restoration Act. The remediation of orphaned oilfield sites, and the plugging and abandonment of wells, have been long-standing regulatory problems in Louisiana, as well as in other oil producing states. In 1993, Louisiana established a public oilfield site restoration fund, and began to authorize the creation of site-specific escrow fund accounts under which the private remediation of oilfield sites could be assured. The presentation will outline the general features of these new programs and their practical impact thus far on general industry practices.

INTRODUCTION

Hundreds of thousands of oil and gas wells have been drilled in the United States. During recent years, oil producing states have struggled with the problems of abandoned oilfield sites. Leases in mature areas tend to be sold from larger to smaller companies, and smaller companies sometimes fail financially before carrying out their obligation to plug and abandon wells and clean up leases. Various estimates regarding the cost of nationwide remediation have been put forth, but the figure certainly runs into the multiple billions of dollars.

Along with other states, Louisiana has undergone significant developments regarding the future remediation of oilfield sites. Historically, Louisiana's regulatory requirements focused on the proper plugging and abandonment of wells, with little specific regulation directed to the surface remediation of sites. These latter issues generally were first addressed in the State's civil caselaw, and involved landowners' demands for site restoration pursuant to private lease

requirements. More recently, however, public law remediation obligations have expanded in significant ways.

I. KEY JURISDICTIONAL STATUTES AND ADMINISTRATIVE AGENCIES INVOLVED IN OILFIELD SITE REMEDIATION

A. LOUISIANA OIL AND GAS CONSERVATION ACT, La. R.S. 30:1 et seq.

This statute is Louisiana's "umbrella" regulatory law governing oil and gas activities, and includes the state's later-enacted statutory site remediation programs, including the 1993 Oilfield Site Restoration Law. The act is administered by the Louisiana Department of Natural Resources, Office of Conservation. This agency exercises general authority over all day-to-day oilfield operations and site restoration activity. By statute, the agency is given the exclusive jurisdiction over the disposal of non-hazardous oilfield waste ("NOW"). Since 1943, the agency's Statewide Order 29-B has contained the core regulations regarding all phases of drilling operations, and now includes specific environmental duties imposed upon well operators.

B. LOUISIANA ENVIRONMENTAL QUALITY ACT, La. R.S. 30:2001 et seq.

This act is administered by the Louisiana Department of Environmental Quality ("DEQ"). DEQ regulations recognize the exclusive authority over NOW given to the Louisiana Office of Conservation. However, DEQ exercises general authority over site remediations involving naturally occurring radioactive material "(NORM"). This jurisdiction will become important particularly in the context of coverage of NORM issues under the 1993 site restoration law. In addition, DEQ has concurrent authority with the Office of Conservation over oilfield site groundwater contamination issues. Finally, the agency exercises general permitting authority over air emissions and water discharges affecting oil and gas operations.

C. LOUISIANA COASTAL WETLANDS CONSERVATION, RESTORATION AND MANAGEMENT LAW, La. R.S. 49:213.1 et seq.

This law is administered by the Department of Natural Resources' Office of Coastal Management and Restoration. That agency oversees a general and individual permitting program covering operations in Louisiana's coastal zone. Oilfield site remediation in these areas, which cover an extensive swath of South Louisiana, will require coordination with this permitting program. A number of general permits already issued under the program may facilitate that process.

II. PREEXISTING REGULATORY STRUCTURE OF OILFIELD SITE RESTORATION REQUIREMENTS

An oilfield site operator's basic cleanup duties are set forth under Office of Conservation Statewide Order 29-B. The agency approaches site remediations under its general "operator of record" doctrine, which is a longstanding policy placing responsibility for general compliance with Office of Conservation regulations on the present operator of record of an oil and gas site. With regard to an operator's P&A obligations, Statewide Order 29-B has long contemplated that the agency can require a bond to assure proper P&A is accomplished, but in practice, that provision has rarely been invoked. More recently, the agency has become involved in approving the down-hole disposal of NORM as part of a general P&A plan.

Statewide Order 29-B also provides specific regulatory parameters for pit closures. Both onsite and offsite disposal methods are set forth. The basic thrust of these rules is the return of the oilfield site to potential agricultural use. Therefore, many specific regulatory limitations on remaining concentrations of waste constituents in the soil are premised on the ability of the soil to sustain future agricultural production.

A. PRECURSOR TO THE 1993 LEGISLATION: ABANDONED OILFIELD WASTE SITE LAW, La. R.S. 30:71 et seq.

In 1986, the Louisiana Abandoned Oilfield Waste Site Law, La. R.S. 30:71 et seq., established procedures under which the Commissioner of Conservation could declare an inactive oilfield waste site "abandoned" for the purpose of undertaking needed cleanup activities and pursuing known responsible parties for

reimbursement. In addition to determining site "inactivity", the Commissioner of Conservation was to consider whether a site had "no financially responsible owner or operator who can be located, or such person has failed or refused to undertake actions ordered by the commissioner . . . ." La. R.S. 30:75.A(4). Upon a declaration that a waste site was indeed "abandoned", the Commissioner then could take physical control of the site for cleanup and closure purposes, and take such legal actions as he deemed necessary to secure the site or to compel cleanup or containment, including the acquisition of easements and rights-of-way, or the exercise of eminent domain. La. R.S. 30:75.D. and E., and 30:78. This statutory cleanup process, however, was left unfunded by the state legislature, and remained essentially dormant.

III. OILFIELD SITE RESTORATION LAW

Act No. 404 of the 1993 Legislature significantly expanded the authority of the Department of Natural Resources ("DNR") to oversee oilfield site cleanups. Under the Oilfield Site Restoration Law, La. R.S. 30:80 et seq., the DNR has begun to administer a new state fund designated for the cleanup of abandoned or "orphaned" oilfield waste sites. DNR also has authority to oversee a broad-based voluntary trust account program for the future cleanup of active sites.

A. OILFIELD SITE RESTORATION COMMISSION

The act established an Oilfield Site Restoration Commission within DNR. Voting members of the Commission include the DNR Secretary and various gubernatorial appointees from the environmental and landowner communities, and from the oil and gas industry. In the past three years, the Commission has begun the task of approving and prioritizing the funding of cleanups of orphaned oilfield sites. These procedures include requirement for site assessments to be performed for orphaned sites, so cleanup costs can be gauged. Moreover, the Commission has arranged for Office of Conservation inspectors to assist in the "ranking" of sites with respect to their need for immediate restoration, i.e., with actively-leaking wells, and the "dirtiest" sites, being addressed first. All actual work is being done by contractors approved by the Commission, and are subject to the public bidding law.

The new cleanup fund, known as the Oilfield Site Restoration Fund, is being financed in part by a levy on oil and gas production and an annual fee on non-producing wells. La. R.S. 30:87. DNR officials estimate that the fund has collected slightly over $9 million through the third quarter of 1996, with approximately $3 million of that already obligated for site remediation projects.

The fund will continue to grow until a $10 million cap is reached; at that time, the law provides that the regulatory levies will be suspended, but then reinstituted if the fund balance dips below $6 million.

B. SITE-SPECIFIC TRUST ACCOUNTS

In addition, under the act the DNR has begun to implement a program under which site-specific trust accounts may be established to govern the future cleanup of oilfield sites when they become "unusable" for further production activity. See April and May 1995 Louisiana Register, codified at 43 LAC Part I, Subpart 2, Chapter 21. These trust accounts may be established in connection with the future (and in certain cases, past) transfer of oil and gas properties, and, once established, La. R.S. 30:88 declares that the transferring party is absolved of any further liability for the cleanup of the site. This liability waiver presumes, however, that the transferring party contemporaneously offers full disclosure of site conditions and otherwise remains in compliance with the act. In addition, this general liability waiver may be read to have been modified by conflicting provisions found in La. R.S. 30:93(2). That section of the new law apparently contemplates that past operators which establish trust accounts may still be liable for a state-led site cleanup that exceeds $200,000 in costs. In any event, and with exception of certain activities related to state-issued mineral leases, this program has not really gotten off the ground.

C. "UNUSABLE OILFIELD SITES" AND "ORPHANED SITES"

The law makes an important distinction between "unusable oilfield sites" and "orphaned sites". An unusable oilfield site is a site which "has no continued useful purpose for the exploration, production, or development of oil and gas and for which a responsible party can be located." (Emphasis added.) On the other hand, sites which do not meet this criterion are classified as "orphaned oilfield sites", and are subject to cleanup using public funds. This latter regulatory status must be declared by the Office of Conservation after efforts are made to notify the last operator at his last known address. Acting pursuant to La. R.S. 30:91, the DNR's Office of Conservation has already declared, through periodic publications in the Louisiana Register, several thousand sites as "orphaned" and deserving of site remediation. Finally, the law specifically provides that "the owner of the property upon which an oilfield site is located [i.e., the landowner] shall not be responsible for site restoration" unless the landowner otherwise meets the definition of an actual "operator". La. R.S. 30:91(c).

D. CLEANUPS BY "RESPONSIBLE PARTIES"

Cleanups of "unusable sites" are first expected to be performed by the "responsible party." In keeping with past regulatory practice, this term is defined as "the operator of record according to the office of conservation records, who last operated the property on which the oilfield site is located at the time the site is about to be abandoned, ceases operation, or becomes an unusable oilfield site . . ." In addition, the definition also includes the operator's "partners and working interest owners." A "working interest owner" is "the owner of a mineral right who is under an obligation to share in the cost of drilling or producing a well on the oilfield site." La. R.S. 30:82(9).

If the responsible party for a site for which a trust account has been established completes a satisfactory cleanup, he may then seek to recover the balance of the trust fund account.

E. COST RECOVERY ACTIONS

If a state-led site cleanup is conducted, the new law directs the DNR Secretary to seek to recover all costs from "any party who has operated or held a working interest" in the site, or who is otherwise determined to be responsible for cleanup. For any oilfield site transferred prior to May 1, 1993, an earlier transferring party will not be liable for restoration costs if those costs do not exceed $200,000. For other sites subject to a trust account, the law specifies that all funds in the account will be used first, and if those funds are insufficient for full restoration, the Oilfield State Restoration Fund shall provide funds not to exceed $200,000. If the funds for restoration are still insufficient, the DNR Secretary may file suit against the former operators and working interests to make up the deficiency. As discussed above, a narrow set of criteria allowing for exemptions from liability (mainly directed at parties which correctly utilize the new trust fund procedures) may apply. In any event, La. R.S. 30:93(A)(3) provides that former operators are to be held responsible in "inverse chronological order" from the time of the site's abandonment. The DNR has not yet, however, began to file cost recovery actions under these provisions, although there may be eventual public pressure to do so.

F. SIGNIFICANT PENALTIES FOR NONCOMPLIANCE

In addition to the cost recovery procedures, the new law added provisions for (i) civil penalties up to $25,000 a day against operators found in noncompliance with the act's provisions, and (ii) the suspension of a company's statewide operating authority, all well allowables, and all pending permit applications before the Office of Conservation.

G. GENERAL OBSERVATIONS

One critical question originally left unanswered by the act is whether site assessments should address the issue of NORM contamination. As discussed earlier, NORM cleanups are regulated by the State's Department of Environmental Quality, at times in conjunction with the Office of Conservation's P&A programs. If the new legislation was to achieve its goal of quantifying, and capping, remediation costs associated with the transfer of an oilfield site, it seemed that potential NORM remediation expenses must be included within the scope of the trust fund program. The Oilfield Site Restoration Commission has since recognized these concerns, and is now requiring that potential NORM cleanup expenses be included within the site assessments conducted at orphaned sites.

Moreover, the act could eventually spur the expansion of the "environmental site assessment" industry. Site assessments in conjunction with the establishment of site-specific oilfield site trust accounts are expected to be conducted by contractors approved by the state. These assessments are to be performed within one year of a site transfer, and will allow for a good faith "best estimate" of the future cost of anticipated site cleanup and abandonment activity, based on the present condition of the site. That estimate will then be used by DNR in setting trust account amounts. (Methods of funding the trust fund account may be proposed by the affected parties, but must be approved by the DNR Secretary.) The expected cost for any site's cleanup is expected to be continually monitored, however, and modifications to the requisite trust account amount over time can occur. Accordingly, if this site-specific account program ever becomes widely utilized, the administration of the program will require many difficult technical decisions with important economic consequences, and will no doubt present a real challenge to the DNR staff.

Finally, it should be noted that this new legislation was, in part, a joint effort by government and industry to address, on the <u>state</u> regulatory level, the significant problem of abandoned oilfield waste site remediation. The legislation may also be seen as a partial response to the Interstate Oil and Gas Compact Commission's ("IOGCC") continuing critical review of the adequacy of state oilfield waste management programs, a review which has remained sensitive to the

federal government's potential regulatory interest over oilfield wastes, and the Environmental Protection Agency's ("EPA") earlier decision to exempt oilfield waste from the definition of "hazardous waste" under the Resource Conservation and Recovery Act ("RCRA"). By enacting this new law to come into line with other states' recent efforts, Louisiana helps the oil producing states' arguments against Congressional expansion of EPA's regulatory jurisdiction over oilfield waste site cleanup, either under RCRA or the Superfund program.

ISSUES AND SOLUTIONS IN INTERNATIONAL EXPLORATION AND PRODUCTION: The Role of Environmental Law

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This paper considers the role and impact of environmental law regarding international oil and gas exploration and production (E&P) activities. It inquires how environmental law contributes to solutions of environmental issues in E&P operations. Key driving forces underlying the proliferation of environmental regulations and standards around the world are considered and identified. Similarly, recent developments in environmental law relevant to international E&P activities are briefly discussed. To illustrate the role of environmental law, some of its principal strengths and weaknesses are identified. To this end, examples from key petroleum producing countries in Asia, Africa, Europe and Latin America are provided.

The paper argues that environmental law is becoming an important comparative assessment factor in E&P projects affecting all aspects of activities, from planning and permitting to exploration, production and abandonment. It is further argued that while environmental law often results in higher project costs which may lead to the termination of certain marginal projects, its overall impact is not as negative as it is sometimes made out to be. The proliferation of environmental law, in fact, can provide for clear goalposts and contractual stability and offers incentives to improve operations, to protect the environment and to improve profitability. That said, there are numerous cases where environmental law has been an obstacle to E&P and even its stated objective of environmental protection. In most cases this has been due to poor implementation and enforcement, particularly though not exclusively in developing countries. Poor drafting of legislation and lack of consultation with industry and other stakeholders can contribute to these problems. While acknowledging that environmental law on its own is unlikely to be able to offer effective solutions, it is argued that other instruments such as voluntary and market-based mechanisms are also unlikely to offer comprehensive solutions. The most promising approach, therefore, will be a mix of prescriptive rules and regulations and goal setting, market-based mechanisms. The paper concludes by underlining the fact that the proliferation of environmental law will continue and that, for better or for worse, environmental law will have to be part of the solution to environmental problems related to E&P.

INTRODUCTION

Oil and gas exploration and production (E&P) activities are associated with a variety of environmental impacts, primarily at local and regional level. In many parts of the world, however, E&P operations are not subject to stringent environmental controls. This is beginning to change. Increasingly, host governments are beginning to consider the environmental viability of E&P activities and to adopt more stringent legislation. International oil companies, consequently, are confronting demands for improved environmental performance. They are also facing a proliferation of policies, laws, guidelines and standards applicable to their operations and, as a result, increased potential legal and financial liabilities (1).

The purpose of this paper is to examine the role and impact of environmental law vis-à-vis international oil and gas E&P activities and to inquire how environmental law contributes to solutions of environmental issues in E&P operations. To this end, the paper considers and identifies:

- Key driving forces regarding the world-wide proliferation of environmental regulations and standards.
- Strengths and weaknesses of environmental law.
- Recent trends in environmental law relevant to international E&P.

Where appropriate, examples from key petroleum producing countries in Asia, Africa, Europe and Latin America are provided. The focus of this paper is on environmental and related business problems arising from E&P operations affecting the industry's "license to operate" and the role that environmental law plays in solving these problems. Particular emphasis is placed on trends in developing countries. Solutions, of course, can be either short or long term in nature and hence can vary considerably in both scope and cost. In this context, finding solutions means finding ways of preventing environmental degradation from E&P (to the extent this is possible for any extractive industry), of controlling pollution once it has occurred, and ensuring that core business interests ("licence to operate", profitability) are respected.

THE LEGAL FRAMEWORK OF E&P ACTIVITIES

The legal framework regarding international E&P activities consists of local, national, regional and international laws and administrative regulations and their application by governments to achieve environmental objectives. In all countries, there is a mixture of these instruments and requirements. In addition to these "hard law" requirements, there is so called "soft-law" consisting of guidelines and non-binding instruments that may potentially evolve into legal standards, such as international conference declarations, and government and industry guidelines (2).

International environmental legal instruments cover subjects considered to be "global" in scope, as well as those traditionally considered domestic. Global issues include marine pollution and, more recently, atmospheric pollution and the conservation of biodiversity. Increasingly, however, international law is addressing topics traditionally seen to be domestic in scope, such as the conservation of species, habitats and ecosystems (3).

Among the growing body of international law on these subjects, there are several treaties, conventions and non-binding international agreements which are of particular importance to the international E&P industry. These include:

- ***1978 MARPOL Protocol:*** The Protocol deals with vessel source pollution and sets specified waste disposal standards for mobile offshore drilling units.

- ***1982 UN Law of the Sea Convention (LOSC)***: Although the LOSC does not directly address pollution from offshore E&P operations, it requires, *inter alia*, coastal states to adopt and enforce laws and regulations in respect of marine pollution arising from sea-bed activities, including E&P.

- ***1992 Convention on Biological Diversity (Biodiversity Convention):*** The main objective of the Convention is to conserve biological diversity. This will require increased consideration of ecosystems and nature conservation and will add to pressures to declare sensitive areas off-limits to E&P.

- ***1992 Framework Convention on Climate Change (FCCC)***: The FCCC requires signatories to adopt measures to reduce emissions of greenhouse gases such as carbon dioxide and methane. Though the FCCC does not lay down specific requirements applicable to E&P operations, it has prompted a process of rule-making affecting energy use in all industry sectors.

- *Agenda 21*: Agenda 21, adopted at the *1992 United Nations Conference on Environment and Development* (UNCED), provides an international programme for achieving sustainable development. C*hapter 17:30* calls for additional measures to control degradation of the marine environment from sea-based activities. Specifically, States are called upon to assess existing regulatory measures regarding pollution from offshore oil and gas platforms.

- ***1992 Rio Declaration on Environment and Development***: Principle 11 of the Rio Declaration, adopted at UNCED, requires states to enact effective environmental legislation. It states that "environmental standards, management objectives, and priorities should reflect the environmental and developmental context to which they apply, recognizing that standards applied by some countries may be inappropriate and of unwarranted economic and social cost to other countries, in particular developing countries."

- ***UNEP Regional Seas Programme***: A number of regional conventions covering areas such as the Mediterranean, the Caribbean, South East Asia and the Arabian

Gulf have been adopted under UNEP's auspices. Most of these contain provisions which are generally applicable to offshore E&P activities. A minority specifically address E&P activities by means of supporting protocols on sea-bed activities. To date such protocols have been adopted for the Arabian Gulf (*1989 Kuwait Protocol)* and the Mediterranean (*1994 Sea-bed Protocol*). Outside UNEP's framework, stringent regulatory requirements are imposed on offshore E&P activities in the North Sea and the Baltic.

Other important instruments include the *1971 Convention on Wetlands of International Importance* (Ramsar Convention) which provides for international mechanisms for the declaration of national wetlands which, once declared, can result in land-use restrictions and the *1989 Convention on Transboundary Movements of Hazardous Wastes* (Basle Convention).

DRIVING FORCES

E&P activities are coming under growing public scrutiny and oil and gas companies are facing increased demands, both at home and abroad, to improve their environmental performance. Around the world, environmental laws are proliferating, even in countries where one would least expect it. For example, Angola has drafted strict environmental regulations for upstream activities, though implementation has been delayed by the civil war (4). Elsewhere, countries such as Cambodia, Laos and Vietnam are in the process of adopting environmental legislation. Vietnam, in fact, recently drafted environmental regulations for offshore E&P (5). A similar trend can be observed in Latin America and other parts of the world.

Although implementation and enforcement of environmental law varies considerably within and between countries, particularly in the developing world, environmental law is rapidly becoming an important comparative assessment factor in upstream petroleum investment. Numerous factors are driving the proliferation of laws and standards. Some derive from moral and ethical considerations whereas others are legal and commercial in nature. Increased public pressure, fueled by media coverage and litigation, add to this trend. Serious pollution incidents, such as the *Exxon Valdez,* can also add to existing political pressure for law reform.

Alongside developments in international environmental law, the most prominent means of proliferation is through the assistance provided to developing country governments in drafting environmental legislation. The sources of this assistance are diverse and include:

- ***National Governments:*** Many governments (e.g. US, Norway) assist developing countries in drafting legislation, frequently in the belief that such assistance benefits their own industry and environmental technologies.

- ***Non Governmental Organizations (NGOs):*** NGOs active in this field include the Worldwide Fund for Nature (WWF) and the World Conservation Union (IUCN). Some, such as the IUCN, have issued guidelines on E&P in tropical rainforests (6).

- ***International Governmental Organizations:*** Some institutions such as UNEP assist governments in drafting legislation. UNEP, in fact, is preparing guidelines for E&P activities.

- ***International Financial Institutions:*** Institutions active in this field include the World Bank and the International Finance Corporation (IFC). The World Bank, for example, has its own E&P guidelines (in the process of being updated). It also has detailed requirements for EIAs and routinely requires projects which it funds to comply with its environmental guidelines. Moreover, it assists governments in developing environmental laws and policies.

- ***Industry Associations:*** International and national industry associations such as the E&P Forum and the American Petroleum Institute (API) contribute to the proliferation of environmental laws through issuing environmental guidelines. The E&P Forum, for example, has issued guidelines on waste management and E&P operations in tropical forests and mangrove areas.

Oil companies contribute to this process as well, primarily through application of their world-wide operational practices. Advances in telecommunications (internet, faxes etc) serve as another mechanism for the dispersion of environmental information, especially on legislative trends in North America and the European Union.

It is also noteworthy that environmental concerns have broadened to encompass the international banking and insurance sectors. Moreover, organizations such as the International Standards Organization (ISO) and its regional and national counterparts are preparing technical and management standards, the most important of which is the ISO 14000 Series on environmental management systems. Although these standards are not regulatory, many believe that they will influence environmental law formation in many countries (7).

THE ROLE OF ENVIRONMENTAL LAW

Environmental law represents one of several instruments to improve environmental quality and achieve stated policy goals. Other instruments include economic and fiscal mechanisms and voluntary instruments. On its own, of course, environmental law cannot solve all environmental problems arising from industrial activities. Nevertheless, it is an important tool and, to this day, is the preferred method used by governments around the world.

In its constitutional role it can provide mechanisms for settling disputes and supervising the implementation of treaties. Its regulatory and prescriptive role can also embody necessary protective measures and provide for flexible procedures for amending and updating these as required (8). More generally, environmental law can provide for clear goal-posts and standards, thereby increasing contractual stability. International environmental law, for its part, provides a mechanism and a framework for more detailed national regulations to be adopted. International law can also be used to secure harmonization and development of national law, facilitate compensation

for environmental damage and provide for offenses, penalties and other sanctions to be employed under national law against polluters (9).

Environmental law can also be used to further the interests of a given country's industry and its environmental technology. The adoption of strict air quality legislation in Germany in the 1980's, for example, led to the development of improved emission control technologies and arguably set the pace for European air quality policy. Similarly, in Argentina, *Resolution 105/92* (which provides the framework for environmental controls in E&P) strongly emphasizes waste management solutions, thereby reflecting the interests of the consultants who drafted it (10).

STRENGTHS AND WEAKNESSES OF ENVIRONMENTAL LAW

General Impacts

It is difficult to generalize about the impact of environmental law. As regards its effectiveness in achieving environmental policy goals, the record is mixed. Certainly, environmental quality has improved in most countries which have adopted environmental legislation. The development of air pollution legislation in Europe since the 1960s, for example, has resulted in significant improvements in air quality. Similarly, the adoption of a new offshore safety case regime in the United Kingdom in the wake of the *Piper Alpha* disaster in 1988, has led to an increased margin of safety offshore and provided a regulatory model around the world (11).

The impact of environmental law on E&P activities is a different matter. The proliferation of environmental law is undoubtedly increasing restraints on the industry, particularly as regards operations in ecologically sensitive areas. It also brings with it increased liabilities in case of accidents or breaches of rules and regulations. In fact, it is difficult to think of any aspect of E&P operations which is not affected by environmental issues and the spread of environmental law. Not surprisingly, regulatory compliance is taking up an increasing proportion of management time in the oil and gas industry.

Indeed, environmental law can drive up compliance costs and lead to costly delays in planning and permitting of activities. In some cases this can stifle foreign investment and stop possible developments in some countries (12). The magnitude of these costs will vary from country to country, depending on the individual circumstances. On the positive side, the spread of more stringent regulatory controls offers companies an incentive to improve their internal operations, to increase efficiency and become more profitable (13).

Environmental targets specified in legislation can be short-term or long-term in nature. Some may be very specific, technical and prescriptive and relatively easy to comply with whereas others may be more general and goal-setting, leaving

more room for industry to find individual solutions. Compliance is relatively easy where companies are applying US or North Sea standards to their global operations. Problems are more widespread where the in-country requirements are strict, too complex and sophisticated to be properly enforced or where there is uneven application. One of the greatest concerns of industry, in fact, is that of uneven application and enforcement of legislation, both within and between countries and regions. For this reason, industry is frequently the greatest advocate of increased harmonization of standards and procedures as this increases the efficiency of operations and compliance and helps to establish a level playing field.

Positive Impacts

While the adoption of stricter controls may lead to the abandonment of certain projects because of the cost of environmental measures, many of the possible developments affected in this way are likely to be marginal in the first place (14). Moreover, there have been major improvements in recent years. For example, the amount of discharged oil in the North Sea has fallen dramatically since the 1960s, in part through better technology but also due to legislative pressures. According to the E&P Forum, operators are also paying more attention to chemicals used offshore. They have now improved the biocides being used, moving away from the more persistent ones. Similarly, the average discharge of oil-based drilling muds (OBMs) in the North Sea has decreased from 90 to 30 tonnes per well since 1986, in large part due to national and regional regulations. In fact, restrictions on discharge of OBMs recently led oil companies to develop water-based muds and synthetic drilling fluids. New regulations have also prompted development of new waste technologies, some of which are being exported or are being applied elsewhere (15).

The proliferation of environmental law has also led to major changes in exploration and seismic techniques. Whereas in the past, companies would cut wide tracks through an area, leaving scars on the land, and build roads which provided a way for "slash and burn" agriculturists to move in (e.g. in Latin America), operators are increasingly being required to use portable gear that can be airlifted in by helicopter. This is an important environmental improvement. Ecuador's new upstream environmental regulations (*Decree No 2982/1995*), for example, makes this a specific requirement (16). By the same token, more and more countries now require an EIA. For example, both Nigeria and Indonesia have recently introduced such requirements for E&P operations (17).

Overall, then, environmental law affects the E&P industry in various ways. It affects general business interests because it is the predominant instrument for achieving sustainable development and because it increases the pressure for environmental change coming from the growing community of "stakeholders" (NGOs, local population, shareholders etc). It also affects E&P- specific interests, primarily through introducing increased operational constraints and costs. This is undoubtedly a challenge to the oil industry and brings with it increased risks and liabilities. That said, current trends in environmental law offer incentives to improve operations, profitability and to protect the environment (18).

Industry Concerns

The world-wide proliferation of environmental law is giving rise to numerous concerns in the E&P industry. These concerns relate primarily to the means of achieving environmental objectives rather than to the objectives themselves. Advocates of non-legislative voluntary instruments and industry self-regulation, for example, often characterize environmental law as a prescriptive command-and-control instrument which leaves industry little flexibility in achieving specified targets.

While acknowledging that prescriptive regulations provide legal certainty and clear goalposts, making inspections easier, critics of the prescriptive approach stress that prescriptive regulations: 1) Lack flexibility and require rewriting when technology changes; 2) Foster a compliance mentality; 3) Promote the status quo; and 4) Are costly and are based on standard solutions. Proponents of self-regulation argue in favour of a goal-setting approach and claim that overt government regulation serves to undermine corporate finance and to focus energies on paperwork rather than pragmatic compliance. The concern for the industry is not, however, limited to the fact that regulation continues to increase. The fundamental problem is the difficulty in accommodating the uncertainty generated by regulatory controls which are unclear, duplicitous or are exercised in an arbitrary manner.

Many of these concerns are well-founded and made on the basis of experience in developed jurisdictions with a long tradition of environmental law. On the other hand, it is unlikely that voluntary and other "alternative" mechanisms on their own will be able to solve all environmental problems. Just like overly stringent command and control instruments, some market-based approaches may be too difficult for certain countries to apply. Economic incentives, for example, require a well developed mechanism for metering pollution which is not always present in developing countries.

Obviously, it is not possible to review all the types of problems that environmental law can give rise to in this paper. Instead, an attempt is made to discuss some of the more important complications that can arise in applying environmental law, particularly in developing countries. These include the following: 1) Over-regulation and/or inappropriate controls; 2) Lack of appropriate legislation; 3) Inconsistent and/or overlapping provisions; 4) Uneven implementation and enforcement; and 5) Administrative complexities.

Most of these problems overlap and can compound each other, thereby affecting the potential of environmental law to be part of the solution of environmental problems in E&P. Each of these problems has, at one point or another, been experienced by most developed countries and it is no surprise that developing countries should be running into similar problems. However, unlike in most developed countries, where legislation evolved over longer periods of time and in response to specific problems, laws are being adopted by developing countries with increasing frequency, in response to accelerating environmental

degradation and external pressure from other governments and international organizations. In some cases this has led to the adoption of regulations which are too complex and costly for the host government to enforce. Given the widespread lack of technical expertise and ability to enforce regulations, the task of implementation is often left up to foreign oil companies, for better or for worse.

Overregulation

In 1991, for example, Venezuela adopted the *Penal Environment Law* (PEL). The law is complemented by a series of implementing decrees providing for specific standards. As it happens, the PEL gave rise to a number of problems. Firstly, the penalties provided for by the law are very severe. Secondly, enforcement of the law is placed in the hands of the criminal courts, thereby leaving open the possibility of imposing prison sentences in cases where an offense has been committed for reasons of negligence, imprudence or inobservance of the law. Moreover, some of the standards provided for are very stringent. Air quality standards, for example, are based on South Californian norms (19). Critics claim that this approach is not appropriate, particularly in view of the economic situation in Venezuela today.

A similar problem occurred in Egypt when the government adopted the *Environment Law No 4/94* and its supporting *Executive Regulations* in 1995. These provide for very stringent environmental standards which prompted some companies to threaten to withdraw from Egypt. Produced water discharge standards, for instance, have been set at 15ppm, even though the recommended limit value set out in the *1994 Mediterranean Seabed Protocol* is 40ppm. Moreover, the standards were more stringent than those being drafted by the Egyptian National Oil Company (EGPC) at the time (20).

There are many factors contributing to the adoption of inappropriate legislation including lack of consultation, corruption and insufficient environmental baseline data. All of these can cooincide and it is seldom that any one is in evidence in isolation.

Lack of Appropriate Legislation

The opposite problem, underregulation and the lack of clear goalposts and standards, can also result in increased costs and give rise to legal problems in the future, particularly if disputes over liability for past pollution occur. The danger of arbitrariness on the part of the government may also increase. This can lead to costly delays in permitting. In these cases, environmental law has an important function to fulfill.

Lack of clear legislative standards and fears over potential liabilities attached to the aquisition of existing acreage in Argentina, for example, was one of the main reasons why the Argentine Petroluem Institute, with the backing of most foreign operators, drafted E&P-specific environmental guidelines in 1992.

The government subsequently translated these guidelines into *Resolution No 105/92* which forms the basis for environmental control of E&P operations in Argentina today (21). The resolution and its supporting regulations aim to provide an integrated environmental regime for all stages of E&P operations and represent one of the first attempts to implement a single regulatory instrument in this field. The Argentine move is significant and has influenced regulatory developments elsewhere in Latin America (e.g. Bolivia and Peru). More recently, in Italy, lack of specific EIA legislation affected operations. Although the EIA requirement was formally extended to E&P in 1991, failure to adopt environmental norms resulted in delays of up to 2 years in the processing of applications for onshore exploration permits. The situation was not resolved until March 1994 when *Decree No 526/1994* on EIA was adopted (22).

Similarly, in Ecuador, the common perception that non-interference by government was the ideal operating ground for oil companies proved incorrect. In fact, the regulatory vacuum prior to 1992 (when E&P-specific environmental regulations were adopted) led to increased uncertainty and required civil servants to take on responsibility in individual cases. As it happened, this held up Conoco's decision to develop five oil fields in Block 16 in the Oriente jungle, and may also have been a factor in its decision to finally withdraw from Ecuador in 1991 (23).

Overlapping and Ambiguous Provisions

In some countries, problems have arisen due to overlapping and ambiguous legislative provisions. In some cases, in fact, it is difficult even to determine what laws apply. In Algeria, for example, the precise scope of applicable legislation is difficult to determine, in part due to frequent administrative changes and the apparent lack of repeal of previous, outdated legislation. Determining administrative competencies and legal requirements is also made difficult because of overlapping administrative provisions and, in some cases, apparant contradictions between old and more recent decrees on the same subject matter. Similarly, amendments to legislative provisions are sometimes made in other sectoral legislation, thereby complicating the task of regulatory tracking.

The matter is made more complex due to the dominant and to some extent overlapping role of Sonatrach, the national oil company vis-à-vis the Ministry of Energy and Mines and the Ministry of Interior which is, *inter alia*, responsible for environmental protection in Algeria. It is understood that in a number of cases this has led to costly delays in permitting. Lack of E&P specific standards and the case by case approach used by the competent authorities in assessing projects, has added to existing uncertainties over terms and conditions. In some cases this has prompted companies to negotiate separate arrangements, for example on waste management, with the national and local authorities. As a result, legal requirements and conditions can considerably from site to site.

Alongside the problem of overlapping and contradictory legal requirements, which can occur in many countries, the main problem lies in the uneven implementation and enforcement of environmental law. One of the underlying causes of this is lack of financial or political commitment to implement environmental legislation. Tensions between oil and gas agencies (who have traditionally held the "environment portfolio" regarding hydrocarbon activities) and the newly emerging environmental authorities add to and illustrate these problems. In a number of countries including Indonesia, Malaysia and the Phillipines, the enforcement authorities are underfunded, overstretched and/or lacking in technical expertise. In many cases, therefore, industry itself is in charge of enforcing standards (24).

LEGISLATIVE TRENDS: CONDITIONS FOR SOLUTIONS

The size and geographical distribution of international E&P activities will be determined by a variety of factors, some more important than others, including oil prices, technology, geological prospects in various parts of the world, political stability in host countries, and the policy and regulatory environment in the countries where major hydrocarbon reserves are found (25). In this context, environmental protection is rapidly becoming an important comparative assessment factor. In some instances the spread of environmental law may push up project costs and contribute to the termination of marginal plays. On the other hand, environmental law by itself is hardly going to alter overall trends in international E&P. Some markets, in fact, are too attractive for companies to ignore, regardless of environmental or legal constraints. Moreover, given the importance of E&P to the economies of many developing countries, governments will be reluctant to jeopardise petroleum investment.

That said, the proliferation of environmental controls and standards and the trend towards more comprehensive environmental legislation is not going to go away. While many countries still lack systematic environmental regulation and administrative capacity, and full implementation of "Agenda 21" is still some way off, the focus on sustainable development and environmental protection will add to pressures on governmental authorities to improve environmental protection.

An important prerequisite for environmental law to contribute to the solution of environmental problems will be the appropriateness of the controls to the country and issue involved. In keeping with Principle 11 of the 1992 Rio Declaration, some observers claim that for many developing countries, it may be advisable to incorporate well-designed environmental provisions into the model and individual contracts rather than to pass new, comprehensive and costly environmental laws (26). Simply transferring developed-country standards to developing countries, in other words, may not always be effective. That said, the internationalisation of environmental rules and regulations is set to continue.

On the other hand, there are a variety of trends in environmental law which, subject to sufficient political and economic backing, promise to provide a better basis for environmental protection in E&P ventures in the future. Of particular interest in this context is the tendency to adopt E&P-specific

environmental regulations. In Latin America, countries such as Argentina, Bolivia, Ecuador and Peru have followed this path. Elsewhere, Angola and Vietnam have drafted similarly structured regulations. The advantage of this approach is that it allows for more industry-specific standards. Similarly, it provides operators with clear goalposts and allows for a mix of goal-setting and prescriptive approaches (27). The objectives are usually set in consultation with industry and are seen by many as being superior to the traditional contract and permit based-systems.

Other important trends at national and international level likely to affect the propensity of environmental law to contribute to solving environmental and related business problems in E&P include:

- The merging of environmental controls with health and safety provisions, the adoption of integrated permitting regimes and the more widespread use of voluntary and market-based instruments.

- The consolidation of administrative competencies into single agencies and more emphasis on enforcement, stricter penalties and liabilities.

- Increased emphasis on environmental impact assessment and nature conservation.

- A continuation of the trend towards zero-discharge regimes and increased emphasis on waste minimisation at all stages of E&P.

While the precise impact of these trends remains to be seen, it is difficult to see how environmental law will not be part of the solution. On its own, of course, it is unlikely to be able to provide answers to all the problems. However, it is far from clear that "soft law" instruments and market-based approaches will be able to provide satisfactory answers either. The most promising approach will be a combination of prescriptive and goal-setting regulations. In the event, much will depend on improving the application of existing regulations and consolidating existing regulatory and administrative arrangements.

Alongside the existence of appropriate and enforceable standards, there is a need to improve and consolidate existing administrative arrangements. In some cases this may necessitate the separation of responsibility for environmental protection from that of promoting petroleum investment. Finally, the existence of appropriate sanctions and the political will to enforce these is important. If there is no risk of penalty then environmental regulations, even if on the law books, will not be heeded. This in fact, is a prerequisite for establishing a level playing field. Timely consultation between all interested parties, particularly between companies, government agencies, environmental activists and the local population is a further prerequisite for effective environmental law solutions.

REFERENCES

1. Armstrong, Kit, "The Challenges of Being Green: Environmental Issues and Strategies for International Oil and Gas Exploration and Production", presented at the 5th Annual Model International Agreements Workshop Vail, Colorado, June 28-30, 1995.

2. Ibid.; Birnie, Patricia & Boyle, Alan, *International Law & the Environment*, 4. Oxford: Clarendon Press, 1992.

3. World Bank, "International Agreements on Environment and Natural Resources: Relevance and Application in Environmental Assessment", *Environmental Assessment Sourcebook No 10*, (1995) August.

4. Stephenson, M.T. (et. al.), "Building Partnerships in Environmental Regulation", in Proceedings of the *Second International Conference on Health, Safety and Environment in Oil and Gas Exploration & Production*, Jakarta, Indonesia: Society of Petroleum Engineers, Inc, (1994), January, 291.

5. Petroconsultants (U.K.) Ltd, *Environmental Law and Policy Service - Vietnam*, Petroconsultants, (1996).

6. IUCN, *Oil Exploration in the Tropics: Guidelines for Environmental Protection*, Gland, Switzerland: IUCN, (1991).

7. Armstrong, (op cit).

8. Ball, Simon and Bell, Stuart, *Environmental Law*, 75. London: Blackstone Press Ltd, 1991.

9. Birnie, Patricia and Boyle, Alan (op cit), 5.

10. Petroconsultants (U.K.) Ltd, *Environmental Law and Policy Service - Argentina*, Petroconsultants, (1995).

11. International Labour Organisation (ILO), *Safety and related issues pertaining to work on offshore petroleum installations*, 11, Geneva: ILO, (1993).

12. Read, Tony, "Environment: A Shift in Emphasis", *Energies*, 27, 10 - 13, (1996), Spring, 13.

13. Armstrong, Kit, "Promoting Sustainable Development: Strategies for the Exploration and Production Industry", presented at the Second International Conference on Health, Safety & Environment in Oil and Gas Exploration and Production, Jakarta, Indonesia, January 1994, 265.

14. Read, Tony, (op cit).

15. Petroconsultants (U.K.) Ltd, *Overview of Rules and Regulations and Recommended Practices for Operational Discharges from Offshore Oil and Gas Exploration and Production Activities*, prepared on behalf of Ministry of Housing, Physical Planning and Environment (VROM), the Netherlands, for Society of Petroleum Engineers Conference, New Orleans, June 1996.

16. Petroconsultants (U.K.) Ltd, *Environmental Law and Policy Service - Ecuador*, Petroconsultants, (1995).

17. Petroconsultants (U.K.) Ltd, *Environmental Law and Policy Service - Nigeria*, Petroconsultants, (1996); *Environmental Law and Policy Service - Indonesia*, Petroconsultants, (1996).

18. Armstrong, (1994), (op cit).

19. Petroconsultants (U.K.) Ltd, *Environmental Law and Policy Service - Venezuela*, Petroconsultants, (1995).

20. Petroconsultants (U.K.) Ltd, *Environmental Law and Policy Service - Egypt*, Petroconsultants, (1995). It is understood that a 3 year extension of existing controls was agreed with the authorities.

21. Petroconsultants (U.K.) Ltd, *Environmental Law and Policy Service - Argentina*, Petroconsultants, (1995).

22. Petroconsultants (U.K.) Ltd, *Environmental Law and Policy Service - Italy*, Petroconsultants, (1995).

23. Reid, Jan, "Crude Awakening", *Texas Monthly*, 140 - 144, 197 - 204, November (1995); Wagner, Jay, "Growing Emphasis on Environment Necessitates Advance Planning", *American Oil and Gas Reporter*, 18, July (1994).

24. Petroconsultants (U.K.) Ltd, *Environmental Law and Policy Service - Malaysia*, Petroconsultants, (1996).

25. International Labour Organisation (op cit.).

26. Gao, Zhiguo, "International Petroleum Exploration and Exploitation Agreements: a Comprehensive Environmental Appraisal", *Journal of Energy and Natural Resources Law*, 2, 240 - 256, (1994).

Joint and Several Liability Versus

Contribution Under CERCLA: Developing Law

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This paper will evaluate the evolving law of joint and several liability, divisibility and contribution under the Comprehensive Environmental Response, Compensation and Liability Act. The paper will contrast the respective procedural timing for addressing these issues, burdens of proof, litigation strategies and recent case law. Finally, the paper will address recent legislative mechanisms proposed for the purpose of interjecting fairness into the joint and several liability scheme.

A. THE CONTROVERSY

Absent substantial CERCLA[1] reform, courts will continue to wade through the morass of litigation compelled by the need to judicially interpret CERCLA's ambiguous provisions. Recently, courts have addressed the issue of whether or not plaintiffs that are potentially responsible parties ("PRPs") have standing to bring cost recovery claims in addition to or instead of claims for contribution. CERCLA allows litigants to sue potentially responsible parties under its cost recovery provision in Section 107(a)[2] and for contribution under Section 113(f).[3] The evolving case law by which courts have attempted to distinguish the two claims has resulted in a split of authority.

Plaintiffs have numerous reasons for preferring Section 107(a) claims over those under Section 113(f):

1. Joint and Several Liability: Section 107(a) allows parties to impose joint and several liability for cost recovery related to the entire site regardless of degree of fault; whereas, Section 113(f) only provides for contribution according to a party defendant's equitable share.

2. Statute of Limitations: Section 107(a) is governed by a six year statute of limitations for recovery of response costs for remedial actions which runs from the initiation of physical on-site construction of the remedial action at the CERCLA site.[4] Section 113(f) is governed by a three year statute of limitations which runs from the date of a judgment, administrative order or judicially approved settlement.[5]

3. Contribution Protection: Plaintiffs have asserted that Section 107(a) allows the recovery of costs against parties that have settled with the government and received contribution protection.

4. Contribution: Some Plaintiffs have argued that a Section 107(a) suit forecloses a defendant's ability to limit its liability by bringing a counter-claim for contribution under Section 113(f).

5. Transactional: Under Section 107(a), plaintiffs do not have to track down and pursue every PRP in order to recoup the non-settling PRPs' share of response costs.

Defendants have responded that where the plaintiffs themselves are PRPs: a) the plaintiffs are limited to Section 113(f) actions; b) plaintiffs should not be allowed to recover a windfall if plaintiffs seek costs exceeding their proportionate share;

and 3) the burden for paying orphan shares should not be imposed solely upon the defendants.[6]

B. BURDENS OF PROOF AND PROCEDURAL ISSUES

In addition to the issues raised above, Section 107(a) and Section 113(f) claims present differing burdens of proof and procedural postures. For example, a court could deem defendants A, B, and C jointly and severally liable under CERCLA Section 107(a) for response costs arising out of releases of hazardous substances at Greenacre. If defendants B and C were insolvent, defendant A could be liable for 100 % of the total response costs. Under this joint and several liability scenario, the plaintiff must carry only the burden of proving that defendant A is subject to Section 107(a) liability.[7] Section 113(f), however, imposes in addition to the elements of proof of a Section 107(a) claim, the requirements that the Section 113(f) plaintiff prove that it has assumed more than its fair share of cleanup costs and that the parties prove their proportionate fair share of response costs.

Section 113(f) allows the court to consider equitable factors at the court's discretion in allocating response costs between parties. Most courts consider the factors known as the Gore Factors:

1. the ability of the parties to demonstrate that their contribution to a discharge, release or disposal of a hazardous waste can be distinguished;

2. the amount of hazardous waste involved;

3. the degree of toxicity of the hazardous waste involved;

4. the degree of involvement by the parties in the generation, transportation, treatment, storage, or disposal of the hazardous waste;

5. the degree of care exercised by the parties with respect to the hazardous waste concerned, taking into account the characteristics of such hazardous waste; and

6. the degree of cooperation by the parties with Federal, State or local officials to prevent any harm to the public health or environment.[8]

Some courts have noted that the Gore Factors are not exclusive and that they may consider additional factors such as laches, unclean hands, estoppel, caveat emptor,

financial strength, and the contractual relationship of the parties in apportioning costs.[9]

Procedurally, the decision of a party's apportionment usually occurs after a party has been determined to be a responsible party under Section 107(a). For example, in United States v. Montana Pole and Treating Plant, et al. (U.S.D.C. Mont. Civil Action No. CV 91-82-BU-PGH), the government sued various defendants for past costs and a determination of liability for future costs under Section 107(a). The defendants also sued each other and additional parties under Section 107(a) and Section 113(f). The court trifurcated the litigation with the determination of Section 107(a) liability occurring in the first phase, the amount of recoverable response costs in the second phase and cost allocation in the third phase. Other courts have bifurcated CERCLA cases into liability and cost allocation phases.[10]

C. COURT DECISIONS

Courts have generally examined the motivation for asserting Section 107(a) standing in determining whether or not a Section 107(a) plaintiff may proceed.

1. Avoidance of Contribution Protection Clause

No court has allowed a plaintiff to bring a Section 107(a) claim (or a Section 113(f) claim) for matters addressed in a consent decree with the United States for which a defendant has received contribution protection.[11]

2. Six Year Statute of Limitations

Where a plaintiff has sought to avail itself of the six year statute of limitations of Section 107(a), courts are split on whether or not the plaintiff has standing to bring the claim.[12] The courts' rationale for allowing separate Section 107(a) standing turns on whether or not courts determine that Section 113(f) and the Section 107(a) actions are distinct and separate actions. Some courts find that the claims are exclusive and that a party should not be allowed to preserve a time-barred Section 113(f) action for contribution through bringing a Section 107(a) cost recovery claim. In contrast, other courts consider Section 113(f) and Section 107(a) to be overlapping actions which allow parties to pursue both claims subject to differing statutes of limitations.[13]

3. Joint and Several Liability

Most courts have allowed plaintiffs to sue under Section 107(a) where a plaintiff has sought to establish joint and several liability.[14] This approach has been criticized as creating an undue procedural burden in cases where the plaintiff has failed to sue all viable parties.[15] As a practical matter, a defendant may simply remedy the unfairness posed by joint and several liability by bringing a counterclaim and/or crossclaim for Section 113(f) contribution to apportion its liability.[16] This solution, however, places the litigation burden of pursuing additional PRPs on the defendant.

Recently, commentators have noted a "dangerous trend" to disallow Section 107(a) claims where the plaintiff is a PRP.[17] The Tenth Circuit Court of Appeals held in United States v. Colorado & Eastern Railroad[18] with respect to a Section 107(a) plaintiff and defendants that:

> There is no disagreement that both parties are PRPs by virtue of their past or present ownership of the site; therefore, any claim that would reapportion costs between the parties is the quintessential claim for contribution. Furthermore, were PRPs such as [plaintiff] Farmland allowed to recover expenditures in clean up and remediation from other PRPs under § 107's strict liability scheme, § 113(f) would be rendered meaningless.[19]

The court proceeded to disregard the "label" used by the plaintiff to characterize the claim as "one between jointly and severally liable parties" and deemed the action one for an appropriate division of the original payment made by the plaintiff.[20]

Courts have both followed[21] and have declined to follow the rationale of Colorado & Eastern Railroad. The reasons for disagreement vary:

1. Courts have distinguished that a PRP which has not formally admitted liability or been formally adjudicated liable is not limited to a claim for contribution under Section 113(f).[22]

2. Courts have followed *dicta* in Key Tronic Corp v. United States,[23] in which the Supreme Court stated: "the statute [CERCLA] now expressly authorizes a cause of action for contribution in § 113 and impliedly authorizes a similar and somewhat overlapping remedy in § 107."[24]

3. In comparing the text of Section 107(a) and Section 113(f), courts have found that Section 107(a) appears to create a separate and distinct right of action for PRPs.[25]

4. Courts have noted that allowing plaintiffs to go forward would not result in an injustice because the plaintiff could be required to pay its equitable share of response costs in a subsequent Section 113(f) action brought by a defendant.[26]

5. Finally, allowing Section 107(a) claims to proceed furthers the fundamental CERCLA goal of promoting expeditious cleanups.[27]

D. DEFENSES TO JOINT AND SEVERAL LIABILITY

In addition to the Section 113(f) versus Section 107(a) distinction, defendants have also attempted to ameliorate joint and several liability through the assertion of the "divisibility" defense. Under CERCLA, liability is joint and several unless there exists a reasonable basis for dividing the harm.[28] Courts have adopted the Restatement (Second) of Torts approach to divisibility:

§ 433A. Apportionment of Harm to Causes

(1) Damages for harm are to be apportioned among two or more causes where

(a) there are distinct harms, or

(b) there is a reasonable basis for determining the contribution of each cause to a single harm.

(2) Damages for any other harm cannot be apportioned among two or more causes.

§ 881. Distinct or Divisible Harms

If two or more persons, acting independently, tortiously cause distinct harms or a single harm for which there is a reasonable basis for division according to the contribution of each, each is subject to liability only for the portion of the total harm that he has himself caused.

The analysis of what constitutes a reasonable basis for apportionment is intensely factual, but does not require an absolute certainty in reaching a reasonable estimate of apportionment.[29] Nonetheless, courts have noted that

"[w]here defendants bear the burden of proving divisibility, responsible parties rarely escape joint and several liability."[30] Thus far only one court has found that a defendant met the substantial burden.[31]

E. LEGISLATIVE REFORM OF SECTION 107(a) AND SECTION 113(f)

Several commentators have recently called for Congress to correct the judicial confusion caused by the Section 107(a) versus Section 113(f) dilemma.[32] Legislators have introduced multiple bills proposing significant reforms to CERCLA liability. The most likely vehicle for Republican reform of CERCLA is H.R. 2500, the "Reform of Superfund Act of 1995," introduced by Representative Michael Oxley on October 18, 1995.[33] As further discussed below, Mr. Oxley's bill addresses each of the major issues discussed above related to Section 107(a) versus Section 113(f) claims.

1. STATUTE OF LIMITATIONS

Section 107(a) actions for costs related to remedial actions are governed by Section 113(g)(2) under which the six year statute of limitations is calculated relative to the initiation of remedial actions.[34] Section 113(f) claims are currently addressed in CERCLA Section 113(g)(3) which calculates the three year statute of limitations for contribution claims relative to the date of a judgment for recovery of response costs or the date of an administrative order or judicially approved settlement with respect to such costs.[35]

H.R. 2500 resolves the dichotomy of the two statutes of limitations by fusing paragraph (2) and (3) to create a hybrid statute of limitations applicable to both Section 107(a) and Section 113(f) claims. Under H.R. 2500, a PRP could bring an action within the later of the statute of limitations currently provided in paragraphs (2) and (3).[36] Parties would, thus, be barred from bringing claims only where such a claim would have been barred under both statutes of limitations currently applicable to CERCLA claims.

2. CONTRIBUTION ISSUES

CERCLA currently grants "contribution protection" to parties that settle their liability with the United States or a State.[37] Section 113(f)(2) provides as follows:

(2) Settlement

> A person who has resolved its liability to the United States or to a State in an administrative or judicially approved settlement shall not be liable for claims for contribution regarding matters addressed in the settlement.

Id. Plaintiffs have attempted to circumvent the contribution protection afforded in Section 113(f) to recover response costs from parties that have settled with the government by pleading Section 107(a) claims.[38]

H.R. 2500 artfully resolves this issue by inserting the phrase "or any other claims" into the contribution protection framework. The operative language would read as follows, "A person who has resolved its liability...shall not be liable for contribution *or any other claims* by any person..."[39] Thus, the bill extends contribution protection beyond the scope of Section 113(f) claims to eliminate any ambiguity as to the extent of a party's protection from a Section 107(a) claim.

3. JOINT AND SEVERAL LIABILITY

H.R. 2500's language also addresses the dispute over whether PRPs can bring Section 107(a) claims by defining a claim for contribution as a Section 107 action. CERCLA Section 113(f)(1) currently provides that:

> Any person may seek contribution from any other person who is liable or potentially liable under Section 9607(a) of this title, during or following any civil action under Section 9606 of this or under Section 9607(a) of this title. Such claims shall be brought in accordance with this Section and the Federal Rules of Civil Procedure, and shall be governed by Federal law. In resolving contribution claims, the court may allocate response costs among the liable parties as the court deems appropriate...[40]

H.R. 2500 would modify this language as follows:

> Except as provided in paragraph (4),[41] any person who is liable or potentially liable under Section 107(a) may seek contribution from any other person who is liable or potentially liable under Section [107(a)] of this title in a claim asserted under Section 107(a). Such claims shall be brought in accordance with Section 107(a), this Section and the Federal Rules of Civil Procedure, and shall be governed by Federal law. In resolving contribution claims, the court may allocate response costs among the liable parties as the court deems appropriate...[42]

This language falls short of what is required to fully resolve the question of whether PRPs can bring Section 107(a) claims because, it leaves unanswered the question of whether a PRP can impose joint and several liability upon other PRPs in a contribution action. H.R. 2500 specifically defines an action for contribution as a Section 107(a) action, but the bill provides that such an action must be brought in accordance with Section 107(a) AND Section 113(f). How this dynamic would impact claims by PRPs against other PRPs remains unclear.

The proposed language leaves the courts substantial latitude to reconcile the liability structure of the two sections. Far from settling the joint and several liability issue in relation to claims between PRP's, it appears H.R. 2500 would force further judicial consideration of this issue.

4. PROPOSED ALLOCATION PROCEDURES

H.R. 2500 includes a proposed allocation procedure for equitably determining each PRP's liability that would minimize the importance of the joint and several liability debate relative to Section 107(a) versus Section 113(f) claims in those cases where the EPA is driving the remediation. The allocation procedure would be mandatory for any response action involving two or more PRPs for which total costs exceed $ 1,000,000 when a PRP has incurred response costs, resolved its liability to the United States with respect to the response action or received an order pursuant to Section 106 of CERCLA and a PRP requests an allocation in writing.[43] The allocation procedures would be discretionary in all other circumstances.[44]

As the first step in the allocation process, the EPA would conduct a PRP search.[45] The identified PRPs would then vote on a per capita basis and elect a neutral allocator to conduct the allocation process.[46] The allocator would be elected from a neutral list of parties provided by the EPA or from a current list of neutral parties maintained by other non-profit or governmental organizations of comparable standing.[47] The allocator would then conduct the allocation process culminating in the issuance of a written report with a nonbinding equitable allocation of response costs between the PRPs. H.R. 2500 provides equitable factors similar to the Gore Factors for the allocator to consider in issuing its report and instructs the allocator to consider these factors without regard to any theory of joint and several liability. The equitable factors provided in H.R. 2500 include:

(1) the amount of hazardous substances contributed by each allocation party;

(2) the degree of toxicity of the hazardous substances contributed by each allocation party;

(3) the mobility of the hazardous substances contributed by each allocation party;

(4) the degree of involvement of each allocation party in the generation, transportation, treatment, storage, or disposal of the hazardous substances it contributed;

(5) the degree of care exercised by each allocation party with respect to the hazardous substances it contributed, taking into account the hazardous characteristics of the hazardous substances;

(6) in the case of an owner or operator, the degree to which the allocation party caused, contributed to, or consented to the release or threat of release of hazardous substances at the facility;

(7) in the case of an owner or operator, the degree of care exercised with respect to hazardous substances released at the facility, taking into account the characteristics of such hazardous substances;

(8) the cooperation of each allocation party in performing the response action(s) and in providing complete and timely information to the allocator; and

(9) such other equitable factors as the allocator determines are appropriate.[48]

A moratorium on litigation and enforcement would be imposed under the bill from the initiation of the allocation procedures until 180 days after the issuance of the allocator's report.[49] In addition, any action pending at the time of the initiation of the allocation proceedings would be stayed until 90 days after the issuance of the report.[50] PRPs would be left with the ability to settle the allocation of liability among themselves during the pendency of the allocation proceedings and submit this allocation for adoption as the allocation report. If the PRP settlement meets certain criteria, the allocator would then adopt the PRP settlement as the allocation report.[51] After the allocator issues the allocation report, PRPs could resolve their liability to the United States based on the percentage share specified by the allocator.[52]

Because the allocation process would determine each PRP's relative responsibility for response costs as the initial step in the CERCLA liability process, the issue of joint and several liability would lose much of its importance. In situations where EPA enforcement orders or section 107(a) claims by EPA are at stake, the allocation process would solve many of the inefficiencies associated with bifurcated and trifurcated CERCLA litigation.

However, the allocation process leaves the joint and several liability debate alive and well with respect to non-EPA enforcement actions. H.R. 2500 provides that the allocation process "shall not be construed to modify or affect in any way the principles of liability under this title as determined by the courts of the United States."[53] Therefore, the issue of whether PRPs can impose joint and several liability on other PRPs would maintain its judicial significance.

5. POTENTIAL FOR REFORM THROUGH SUPERFUND REAUTHORIZATION

The political considerations of a presidential election year and the strategic posturing by Republicans and Democrats that has accompanied the election continue to hamstring the Superfund reauthorization process. The chances are bleak for Superfund reauthorization to pass prior to end of the 104th Congress.[54] We predict that President Clinton is unlikely to sign an overhaul of the Superfund program in the midst of his efforts to cast the Republicans as anti-environment. In the meantime, the Republicans are not likely to provide environmental ammunition to President Clinton by pressing for Superfund reform prior to the presidential election. Regardless, even if the currently proposed legislation passes, H.R. 2500 does not conclusively settle the question of whether a PRP can impose joint and several liability on other PRPs. Accordingly, final resolution of this question will require further judicial scrutiny of the Section 107 and Section 113 liability schemes.

References Cited

1. Comprehensive, Environmental Response, Compensation and Liability Act ("CERCLA"), 42 U.S.C. §§ 9601 - 9675 (1995).

2. 42 U.S.C. § 9607 (1995).

3. 42 U.S.C. § 9613 (1995).

4. 42 U.S.C. § 9613(g)(2) (1995).

5. 42 U.S.C. § 9613(g)(3) (1995).

6. Ann Alexander, Standing Under Superfund §§ 107 and 113: Avoiding the Error of the Blind Man and the Elephant, 10 Toxics L. Rep. (BNA) 155 (July 12, 1995) ("Standing Under Superfund"); Pneumo Abex v. Bessemer and Lake Erie Railroad Co., 921 F. Supp. 336, 346 (E.D. Va. 1996); Town of New Windsor v. Tesa Truck, Inc., 919 F. Supp. 662, 681 (S.D.N.Y. 1996).

7. Section 107(a) plaintiffs must prove that a PRP defendant falls within a category of responsible parties under Section 107(a); the site is a "facility;" a release or threatened release of hazardous substances occurred; and the response costs sought by the plaintiff are consistent with the National Contingency Plan.

8. 126 CONG. REC. 26,779, 26,781 (1980); e.g., United States v. Sequa Corp., 3 F.3d 889, 901 (5th Cir. 1993).

9. E.g., Alcan-Toyo American, Inc. v. Northern Illinois Gas Co., 881 F. Supp. 342 (N.D. Ill. 1995); Emergency Technical Servs. Corp. of Illinois v. Morton International, No. 92 C 3376 (N.D. Ill. 1-31-94) 1994 U.S. Dist. LEXIS 899.

10. See, e.g., United States v. Stringfellow, 661 F. Supp. 1053 (1987); United States v. Wade, 653 F. Supp. 11 (E.D. Pa. 1984); United States v. South Carolina Recycling and Disposal Inc., 653 F. Supp. 984 (D.S.C. 1984).

11. See 42 U.S.C. § 9622 (g)(4); see, e.g., United States v. Colorado & Eastern Railroad Co., 50 F.3d 1530 (10th Cir. 1995); Akzo Coatings Inc. v. Aigner Corp., 30 F.3d 761 (7th Cir. 1994); United States v. ASARCO, 814 F. Supp. 951 (D. Colo. 1993); Avnet Inc. v. Allied-Signal Inc., 825 F. Supp. 1132 (D.R.I. 1992); Dravo Corp. v. Zuber, 804 F. Supp. 1182 (D. Neb. 1992), aff'd, 13 F.3d 1222 (8th Cir. 1994); Transtech Industries Inc. v. A & Z Septic Clean, 798 F. Supp. 1079 (D.N.J. 1992); Burlington Northern Railroad Co. v. Time Oil Co., 738 F. Supp. 1339 (W.D. Wash. 1990); United States v. Hardage, 19 C.W.L.R. 131 (W.D. Okla. 1989)

12. United States v. SCA Services of Indiana, Inc., 849 F. Supp. 1264 (N.D. Ind. 1994); United Technologies Corp. v. Browning-Ferris Industries, Inc., 33 F.3d 96 (1st Cir. 1994), cert. denied, ___ U.S. ___, 115 S.Ct. 1176, 130 L.Ed.2d 1128 (1995).

13. United Technologies Corp., 33 F.3d at 103.

14. Richard D. Buckley, Jr., Making a Case for Statutory Amendment to the Comprehensive Environmental Response, Compensation and Liability Act ("CERCLA"): Solving the Section 107/Section 113 Cause of Action Controversy, 31 Tulsa L.J. 851 (Summer 1996) ("Statutory Amendment").

15. See Standing Under Superfund, p. 160; Patricia Lynne Truscelli, Apportionment and Allocation of Liability Under CERCLA: Recent Case Law, CA37 ALI-ABA 99 (February 14, 1996).

16. See Mark A. Stach, Only "Innocent" Parties Need Apply: The Death of the Private Party Recovery Actions Under Superfund?, 20 Wm & Mary Envtl. L. & Pol'y Rev. 33, 43 (Fall 1995).

17. Statutory Amendment, p. 865.

18. 50 F.3d 1530 (10th Cir. 1995).

19. Id. at 1536.

20. Id.

21. See Town of New Windsor, 919 F. Supp. at 681; Johnson County Airport Commission v. Parsonitt Co., Inc., 916 F. Supp. 1090, 1090-95 (D. Kan. 1996); Reynolds Metals Co. v. Arkansas Power & Light Co., 920 F. Supp. 991, 994-97 (E.D. Ark. 1996); Ekotek Site PRP Committee v. Self, 881 F. Supp. 1516, 1521 (D. Utah 1995); Plaskon Electronic Materials, Inc. v. Allied Signal, 904 F. Supp. 644, 651 (N.D. Ohio 1995).

22. Laidlaw Waste Systems, Inc. v. Mallinckrodt, Inc., 925 F. Supp. 624, 630-31 (E.D. Mo. 1996).

23. 511 U.S. 809, 114 S.Ct. 1960, 1965-66, 128 L.Ed.2d 797 (1994).

24. Pneumo Abex Corp., 921 F. Supp. at 345

25. Pinal Creek Group v. Newmont Mining Corp., 926 F. Supp. 1400, 1405-06 (D. Ariz. 1996); Adhesives Research, Inc. v. American Inks & Coatings Corp., 931 F. Supp. 1231, 1238-39 (M.D. Pa. 1996); Bethlehem Iron Works, Inc. v. Lewis Industries, Inc., 891 F. Supp. 221, 225 (E.D. Pa. 1995); Charter Township of Oshtemo v. American Cyanamid Company, 910 F. Supp. 332, 337 (W.D. Mich. 1995); see also Idylwoods Associates v. Mader Capital, Inc., 915 F. Supp. 1290, 1313-14 (W.D.N.Y. 1996).

26. Pinal Creek Group, 926 F. Supp. at 1407; Charter Township of Oshtemo, 910 F. Supp. at 337, Bethlehem Iron Works, Inc., 891 F.Supp. at 225.

27. Pinal Creek Group, 926 F. Supp. at 1408.

28. United States v. Sequa Corp., 3 F.3d 884 (5th Cir. 1993); United States v. Alcan Aluminum Corp., 964 F.2d 252 (3rd Cir. 1992); United States v. Alcan Aluminum Corp., 990 F.2d 711 (2d Cir. 1993).

29. Sequa Corp. 3 F.3d 903; United States v. Chem-Dyne, 572 F. Supp. 802 (S.D. Ohio 1983).

30. Colorado Eastern R.R. Co., 50 F.3d at 1535; O'Neil v. Picollo, 883 F.2d 176, 178-79 (1st Cir. 1989), cert. denied, 493 U.S. 1071, 110 S.Ct. 1115, 107 L.Ed.2d 1022 (1990).

31. Sequa Corp., 3 F.3d at 903-04; see also Acushnet Co. v. Coaters Inc., No. 93-11219-REK (D. Mass. July 24, 1996) (finding defendant not liable under CERCLA where defendant's waste did not cause plaintiffs to incur response costs).

32. See, e.g., Standing Under Superfund and Statutory Amendment supra at notes 6, 13.

33. H.R. 2500, 104th Cong., 2d Sess. (1995). The main Democratic proposal to reform Superfund is H.R. 228, 104th Cong., 2d Sess. (1995) introduced by Representative John Dingell. Mr. Dingell's bill face slim chances of passage because of the Republican control of Congress. Cf., e.g., Superfund: House Democrats' Letter to GOP Continues to Fault Oxley Bill, Negotiations, BNA Daily Environment Report, June 24, 1996.

34. See 42 U.S.C. § 9613(g)(2) (1995).

35. See 42 U.S.C. § 9613(g)(3) (1995).

36. H.R. 2500, 104th Cong. 2d Sess. § 208(2) (1995). H.R. 2500's statute of limitations section provides as follows:

(b) PERIOD IN WHICH ACTION MAY BE BROUGHT. - SECTION 113(G) (42 u.s.c. 9613(g)) IS AMENDED BY STRIKING PARAGRAPHS (2) AND (3) AND INSERTING IN LIEU THEREOF THE FOLLOWING:

"(2) ACTIONS FOR RECOVERY OF COSTS. - (a) EXCEPT AS PROVIDED IN SUBPARAGRAPH (c), AN INITIAL ACTION FOR RECOVERY OF COSTS REFERRED TO IN SECTION 107 MUST BE COMMENCED -

"(i) for a removal action, within 3 years after completion of all removal action taken with respect to the facility, including off-site disposal of any removed materials, except that if physical on-site construction of the remedial action is initiated within 3 years after the completion of all removal action taken with respect to the facility, costs incurred for removal action may be recovered in a cost recovery action brought under clause (ii); and

"(ii) for a remedial action, within 6 years after initiation of physical on-site construction of the remedial action.

"(B) In any such action described in this paragraph, the court shall enter a declaratory judgment on liability for response costs or damages that will be binding in such action or in any subsequent action or actions to recover further response costs or damages. A subsequent action or actions under section 107 for further response costs at the vessel or facility may be maintained at any time during the response action, but must be commenced no later than 3 years after the date of completion of all response action. Except as otherwise provided in this paragraph, an action may be commenced under section 107 for recovery of costs at any time after such costs have been incurred.

"(C) An action by any potentially responsible party against another potentially responsible party for recovery of any response costs or damages must be commenced within the later of -

"(i) the time limitations set forth in subparagraph (A); or

"(ii) where recovery is sought for costs or damages paid pursuant to a judgment or settlement, 3 years after -

"(I) the date of judgment in any action under this Act for recovery of such costs or damages, or

"(II) the date of any administrative order or judicial settlement for recovery of the costs or damages paid or incurred pursuant to such a settlement.".

37. 42 U.S.C. § 9613(f)(2) (1995).

38. See supra note 11 and accompanying text.

39. H.R. 2500, 104th Cong., 2d Sess. § 209(2) (1995).

40. 42 U.S.C. § 9613(f)(1) (1995).

41. Paragraph (4) of this section of H.R. 2500 sets limits on contribution claims:

"(4) LIMITATIONS ON CONTRIBUTION ACTIONS. - (A) THERE SHALL BE NO RIGHT OF CONTRIBUTION UNDER THIS SUBSECTION IN ANY OF THE FOLLOWING CIRCUMSTANCES:

"(I) THE PERSON ASSERTING THE RIGHT OF CONTRIBUTION HAS WAIVED THE RIGHT IN A SETTLEMENT PURSUANT TO THIS ACT.

"(II) THE PERSON FROM WHOM CONTRIBUTION IS SOUGHT IS NOT LIABLE UNDER THIS ACT.

"(III) THE PERSON FROM WHOM CONTRIBUTION IS SOUGHT HAS ENTERED INTO A SETTLEMENT WITH THE UNITED STATES PURSUANT TO SECTION 122(G), WITH RESPECT TO MATTERS ADDRESSED IN THAT SETTLEMENT.

"(B) ANY PERSON WHO COMMENCES AN ACTION FOR CONTRIBUTION SHALL BE LIABLE TO THE PERSON AGAINST WHOM THE CLAIM OF CONTRIBUTION IS

BROUGHT FOR ALL REASONABLE COSTS OF DEFENDING AGAINST THE CLAIM, INCLUDING ALL REASONABLE ATTORNEYS' AND EXPERT WITNESS FEES, IF -

"(I) THE ACTION IS BARRED BY SUBPARAGRAPH (A);

"(II) THE ACTION IS BROUGHT AGAINST A PERSON WHO IS PROTECTED FROM SUCH SUITS PURSUANT TO SECTION 113(F)(2) BY REASON OF A SETTLEMENT WITH THE UNITED STATES; OR

"(III) THE ACTION IS BROUGHT DURING THE MORATORIUM PURSUANT TO SECTION 128 (RELATING TO ALLOCATION).".

H.R. 2500, 104th Cong. 2d Sess. § 209(4) (1995).

42. H.R. 2500, 104th Cong., 2d Sess. § 209(1) (1995)

43. H.R. 2500, 104th Cong. 2d Sess., § 207 (1995).

44. Id.

45. Id.

46. Id.

47. Id.

48. H.R. 2500, 104th Cong., 2d Sess., § 207 (1995).

49. Id.

50. Id.

51. Id. The criteria for the allocator to adopt the PRP settlement are:

(1) the private allocation is a binding allocation of 100 percent of the past, present, and future costs of the response action(s);
(2) the private allocation does not allocate any share to any person who is not a signatory to the private allocation, unless the representative of the fund is a signatory to the private allocation; and
(3) the signatories to private allocation waive their rights to seek recovery of response costs or contribution under this Act with respect to the response action(s) from any other potentially responsible parties at the facility.

52. Id.

53. Id.

54. See, e.g., Chances Remote of CERCLA Bill This Year, Superfund Week, June 7, 1996.

Availability of Insurance Coverage to Pay for Remediation of Environmental Contamination Caused by Petroleum Products

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Abstract:

Clean-up of contamination caused by petroleum products can create overwhelming financial liability for the potentially responsible party ("PRP"). One source of payment for remediation costs is insurance provided by general liability policies issued to the PRP. The availability of insurance coverage under such policies is dependent on the ability of the PRP to prove that property damage began or continued during a policy period several decades past. This paper examines the basic principles of insurance coverage, recent developments in insurance law pertaining to remediation of environmental contamination, and the applicability and admissibility of scientific techniques to prove that property damage occurred during a covered policy period.

INTRODUCTION

Liability for environmental clean-up costs can pose disastrous financial consequences for large and small corporations alike. Remediation of long-term release and migration of petroleum products in groundwater can be particularly expensive. Faced with strict liability under state and federal statutes, the potentially responsible party ("PRP") frequently has little negotiating leverage and must accept, implement, and pay for the remedial action. Under such circumstances, identifying other parties who must share the cost of remediation may be critical to the financial survival of the PRP. One source of recovery frequently overlooked is a party who promised to pay for all damages suffered by the PRP: its general liability insurer from decades past.

Where release and migration of contaminants has occurred over many years, it is possible that some portion of the property damage caused by the release occurred during a period when the PRP had a particular type of insurance coverage in place: a so-called "comprehensive general liability policy," frequently referred to as a "CGL" policy. CGL policies issued during the 1960's and 1970's typically promised to pay the insured for "all sums" which the insured becomes obligated to pay as the result of an "occurrence" which was neither expected nor intended from the viewpoint of the insured. In short, the insurer promised to pay the insured PRP for *all damages* arising out of an occurrence, so long as *some damage* to property occurred during the policy period.

During the remedial investigation process, scientists and other technical professionals are usually called upon to identify the nature and extent of contamination for the purpose of designing an effective remedy. However, when the PRP is seeking to establish coverage under a CGL policy, the *timing* of releases assumes added significance. The scientist will likely be called upon to identify the point source, migratory pathway and transport mechanism of existing contamination for the purpose of expressing an opinion on the question of whether contamination began or continued during a year covered by a CGL policy.

The law of insurance coverage is complex and sometimes arcane. Its complexity is compounded by the fact that the rules of policy interpretation may vary depending on which of the fifty states' laws will control. However, the scientist or other technical professional should be aware of the basic principles governing the availability of insurance to pay for environmental clean-up. The modest goal of this paper is to provide the scientist and technician with a working knowledge of those basic principles so that he can be sensitive to the legal implications of his work on the potential for insurance recovery.

Working Scenario

For purposes of discussion, this paper will assume the following facts, which are entirely fictional: Gasco currently owns and operates a facility where it loads gasoline into tanker trucks. It has owned and operated the facility continuously since 1960. The Gasco facility is located in a heavily industrialized area. In recent years, suburbs have grown up around the Gasco facility. Domestic water wells supply drinking water for the suburbs. Gasco sits above the aquifer which supplies the domestic water wells. In 1970, Gasco removed an underground storage tank. When the tank was removed, it exhibited obvious corrosion and the soil immediately below the tank appeared to saturated with gasoline.

In 1985, the domestic water wells nearest the Gasco plant began to show signs of gasoline contamination. In the ensuing ten years, additional down-gradient water wells have become contaminated with gasoline. Tests have revealed that a single gasoline plume underlies Gasco's property, the property of several other adjacent industrial facilities, and the domestic water wells. The EPA has imposed a "pump and treat" remedy, which will cost approximately $20 million. Gasco has entered into a consent decree agreeing to implement and pay for the remedy. The adjacent industrial facilities have declined to participate in the remedy and have declared bankruptcy.

Gasco had comprehensive liability policies in force during the 1960's. Those policies provided coverage up to $5 million per occurrence per year. After 1969, Gasco ceased purchasing liability insurance. In 1995, Gasco made a claim on its insurers who provided coverage during the 1960's to pay the entire $20 million for the pump and treat remedy.

The insurance companies who issued policies to Gasco in the 1960's have denied coverage, claiming that there is no evidence that there was property damage during the policy periods (i.e., 1960's) which was caused by Gasco's operations.

Do Gasco's 1960 policies provide coverage for the $20 million remedy?

The Comprehensive General Liability Policy

A comprehensive general liability policy insures against damage caused by the insured to a third party. It excludes coverage for damage caused to the insured's own property. Although insurance policies are often lengthy and complex, the most important and basic part of the policy is the "insuring agreement," i.e., the promise of the insurance company to pay for damages for which the insured becomes liable.

Insurance policies vary from insurer to insurer and from insured to insured. However, the insurance industry generally uses standard form insurance policies. By using such standard forms, the insurance industry obtained two main benefits: First, the industry was better able to predict its risk in issuing standard form policies. The industry was able to use actual claims experience under a standard form to set premiums commensurate with the risk being insured. Second, by utilizing standard forms, the primary insurer was better able to "re-insure" the risk, that is, to pass off part of its potential liability to another insurer or group of insurers.

In the 1960's and 1970's, many comprehensive general liability policies utilized standard forms in the "insuring agreement." These standard forms were extremely broad in their coverage and were intended to protect the insured from all damages except those which were intentionally caused by the insured or which the insured expected were substantially certain or highly likely to occur. It is these policies which provide the potential for coverage for long term contamination.

The Insuring Agreement

During the first portion of Gasco's coverage (1960 through 1966), most comprehensive general liability policies contained an insuring agreement which read something like "the insurer will pay on behalf of the insured all sums which the insured shall become legally obligated to pay as damages because of injury or destruction to property as the result of an accident." These policies are referred to as "accident based policies."

Between 1967 and 1970, the insuring agreement probably stated that the "insurer will pay on behalf of the insured all sums which the insured shall be become legally obligated to pay as damages because of property damage caused by an occurrence." The term occurrence was usually defined as "an accident or occurrence, including repeated or continuous exposure to conditions, which results in property damage during the policy period which was neither expected nor intended from the viewpoint of the insured." These policies are referred to as "occurrence based policies."

The definition of property damage typically included "injury to or destruction of property, including the loss of use thereof . . . ." The policy probably specifically excluded damage to the insured's own property.

Remediation Costs As Damages

The first hurdle that Gasco must overcome in proving its claim for coverage is to establish that payment for remediation costs constitutes "damage" under the insuring agreement. Almost all states now recognize costs of reimbursing governments or third parties for remediation efforts "as damages" that the insured is legally obligated to pay as a result of "property damage." A summary of the decisions, both pro and con, on the topic of whether remediation costs are "damages" can be found in *AIU Insurance Co. v. Superior Court,* 51 Cal. 807, 819-20 (1990).

Assuming that Gasco is in a jurisdiction which recognizes remediation costs as damages, it will be able to recover costs of remediation, subject to its ability to prove that property damage occurred during the policy period which was not expected or intended by the insured.

The "Occurrence": Property Damage During the Policy Period

Assuming that Gasco's payment of the remediation costs qualifies as damages under the policy, Gasco must establish (1) injury to property (2) not owned by Gasco (3) that occurred during the policy period and (4) which resulted in damage neither expected nor intended from the viewpoint of the insured.[1]

Was there injury to property not owned by Gasco? In the assumed facts, there appears to be contamination to groundwater that underlies Gasco's property, as well as contamination of groundwater beneath the domestic wells. Is contamination of groundwater "injury to property" within the meaning of the policy? Yes. *See, e.g., AIU Insurance v. Superior Court,* 51 Cal.3d 807, 829 (1990). Is contamination of groundwater beneath Gasco's property damage to "property owned by the insured" so as to be excluded from coverage by the terms of the coverage? No; in most states property owners do not "own" the groundwater beneath their land for purposes of the "owned property exclusion" of the CGL policy. *See, e.g., Intel Corp. v. Hartford Accident & Indem. Co.,* 692 F.Supp. 1171 (N.D. Cal. 1988).

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[1] There is an ongoing debate between insurers and insureds regarding who has the burden of proving that the damage was neither expected nor intended. As a practical matter, however, the insurer usually attempts to avoid coverage by attempting to prove that the insured expected or intended the damage.

Did the injury to property occur during the policy periods 1960 through 1969? Gasco's insurer claims that it did not, presumably because the contamination was first discovered in 1970, one year after Gasco's last policy expired. In order to obtain coverage for the cleanup, Gasco must establish that there was injury to groundwater that commenced or continued between 1960 through 1969.

Gasco can pursue several generally accepted methods of proving that the contamination which caused the gasoline plume began or continued during the covered period. First, Gasco can attempt to establish the timing of the initial leak and the point source of the contamination through computer modeling. The modeling will take into account factors such as infiltration rate, flow direction, velocity, geology, migratory pathways, soil characteristics, and the effect of domestic pumping on groundwater flow. Obviously, the reliability of such modeling is dependent on the amount of information available the scientist and the number of variables which must be tracked in the model. As discussed in detail below, the scientist must be able to state his opinion to some level of certainty that rises above mere speculation.

Gasco can also attempt to establish that the contamination was caused during the policy period by straightforward chemical analysis, conditions permitting. If, for example, the underground storage tank was used to store only a single type of gasoline with particular characteristics (e.g., diesel fuel or unleaded gasoline), it is possible that the chemical composition of the plume can be matched to the type of gasoline stored in the tank. More sophisticated techniques such as gas chromatography can also be used to make the same match and to identify an approximate time of release.

Gasco can also attempt to use more precise methods to further narrow the time of release. For example, use of isotopic analysis of lead additives in gasoline to identify the date of release within 1 to 5 years has recently been proposed *See* R. Hurst, T. Davis, and B. Chinn, *The Lead Fingerprints of Gasoline Contamination,* 30 ENVIRONMENTAL SCIENCE AND TECHNOLOGY 304 (1996).

Because Gasco will rely almost entirely on scientific opinion to prove property damage during the policy period, it must provide evidence which rises to some level of scientific certainty and reliability. The particular level of certainty required will vary depending on the particular jurisdiction in which the case is pending. For example, Federal Rule of Evidence 702 provides in pertinent part that "[i]f scientific, technical, or other specialized knowledge will assist the trier of fact to understand the evidence . . . an expert may testify thereto." Federal courts will generally conduct a preliminary assessment of whether the methodology underlying the testimony is scientifically valid and whether the methodology can properly be applied to the facts in issue. *Daubert v. Merrell Dow Pharmaceuticals, Inc.*, 113 S.Ct. 2786, 2796-97 (1993). In making that determination, federal courts will consider, among other things, whether the technique has been tested,

subjected to peer review, and is generally accepted in the relevant scientific community.

One reported decision has held that gas chromatograph analysis is a generally accepted method of matching oil samples. *U.S. v. Distler*, 671 F.2d 954, *cert. denied*, 454 U.S. 827 (1981). Many decisions have upheld the admissibility of expert opinion based on groundwater modeling. *See, e.g., Sterling v. Velsicol Chemical Corp.*, 855 F.2d 1188, 1199 (6th Cir. 1988). Other decisions have refused to admit expert testimony regarding groundwater modeling, particularly where the underlying assumptions have been invalid or where there is insufficient data to support the model. *See, e.g., Anderson v. Cryovac, Inc.*, 862 F.2d 910 (1st Cir. 1988).

Assuming that the appropriate data is available to Gasco's experts, a simplified version of the scientific opinion on which Gasco will likely base its claim that property damage occurred during the policy period will likely state that "(1) based on available information regarding direction of groundwater flow, the point source of the gasoline in the aquifer is the underground storage tank on Gasco's property; (2) based on the rate of groundwater flow and geology underlying the site, it would take approximately 30 years for gasoline to migrate to the domestic water wells furthest from Gasco's facility; (3) based on age dating of lead isotopes in the gasoline, it was produced between 1964 and 1966; and (4) therefore, it is probable that gasoline first leaked from Gasco's underground storage tank between 1964 and 1966 and has continuously migrated through and into the groundwater since the initial release.

Who Pays What: Trigger of Coverage and Allocation of Damages Among Insurers

Assuming that Gasco convinces the jury that the initial release and property damage occurred between 1964 and 1966, the question remains: which insurers are liable for the costs of the remediation. The answer to this question depends on two variables: the theory of "trigger" applied to the insurance policies and how losses are allocated among successive insurers liable for the same damage.

The concept of trigger is an important one for determining which policies must respond to Gasco's claim for damages. The term "trigger" is a shorthand way of referring to the particular methodology for determining which insurers must pay for damages caused by a progressive or continuing injury. The scientist or technician who is assisting with an insurance claim should be familiar with the basic theories of trigger.

In Gasco's case, the injury began in 1964 and continued at least through the end of the period of insurance, i.e., 1969. Which policies can be called upon to reimburse Gasco for the $20 million remediation? In environmental contamination cases, there are two likely alternatives: losses could be assigned to the policy(ies) in effect (1) during all periods when damage occurred (1964-69), or (2) when the damage was discovered (1970). Depending on which "trigger" theory is applied, Gasco could recover $20 million or nothing.

Under the so-called "continuous" trigger, property damage that is continuous or progressive in nature triggers coverage under each policy that is in effect during any year in which property damage occurred. Thus, Gasco's pre-1964 insurers would not be held liable for Gasco's remediation costs because there was no property damage during those years. However, all insurers with policies in effect between 1964 and 1969 would be liable for Gasco's remediation costs because of the expert testimony that the damage commenced in 1964 and continued through 1969. *See, e.g., Montrose Chemical Corp. v. Admiral Ins. Co.*, 10 Cal.4th 645, 675 (1995)(adopting continuous trigger for environmental contamination). Thus, under the continuous trigger theory, the ability to establish a date of initial release and continuing property damage is extremely important to the insured.

Under the so-called "manifestation" theory of trigger, the only insurer called upon to pay damage is the insurer whose policy is in effect when "appreciable damage occurs and is or should be known to the insured." *Id.* In Gasco's case, damage was first discovered, or became "manifest," when the underground storage tank was replaced in 1970 – a time when Gasco had <u>no</u> insurance coverage in place.

If Gasco sues in a jurisdiction which adopts the continuous trigger, it will likely recover the entire $20 million in remediation costs (after paying its deductible). If Gasco sues in a jurisdiction which applies the manifestation trigger, it will likely recover nothing from its insurer.

Assuming that Gasco prevails on the continuous trigger theory, its insurers will likely make several more arguments to avoid paying the full $20 million of remediation costs. The insurers may seize on the testimony of Gasco's expert that the damage was continuous from and after 1964 to the present. The insurers might argue that the damage should be allocated proportionately over the 32 year period of continuous damage (1964-96). Since Gasco was uninsured from 1970 through 1996, the insurers may argue that Gasco must bear 81% of the loss (26 uncovered years divided by 32 years of total damage).

Such an argument is contrary to the plain language of most CGL policies. Most policies state that the insurer will pay "all sums which the insured shall become legally obligated to pay as damages because of property damage caused by an occurrence." Gasco can establish that there was a single occurrence which

triggered all policies between 1964 and 1969. Each insurer thus should be liable to pay "all sums" (i.e., damages) which the insured must pay as the result of the occurrence, regardless of the fact that Gasco was uninsured during some period when the injury was continuing. The California Supreme Court has recently noted the "settled rule that an insurer on the risk when continuous or progressively deteriorating injury first manifests itself remains obligated to indemnify the insured for the entirety of the ensuing damage." *Montrose Chemical Corp. v. Admiral Ins. Co.*, 10 Cal.4th 645, 686 (1995). A more recent appellate decision has further explained the application of the "all sums" language as follows:

> Once an injury triggers coverage . . . the insurer must indemnify the insured for "all sums" which the insured becomes obligated to pay, whether during the period of the policy issued by the insured or after; the policy language does not limit the insurer's liability to "all sums which the insured becomes liable to pay during the policy period."

Stonewall Ins. Co. v. City of Palos Verdes, 46 Cal. App. 4th 1810, 1855 (1996).

Thus, as between Gasco and its insurers, the insurers should be required to pay the entire $20 million of remediation costs. The insurers are free to argue among themselves how that $20 million should be allocated between insurers. Gasco is not required to "allocate" a portion of the damage from a continuous injury to an uncovered period.

Even if Gasco had "gaps" in its coverage, e.g., it had policies from 1960-65 and 1968-69, it should not be obligated to accept allocation of any of the damages from 1966-67 when it had no coverage. Such an argument was advanced by insurers in the asbestos litigation, who claimed that the insured should bear the risk for gaps in its coverage. The appellate court firmly rejected that argument, stating

> once coverage is triggered, the insurer's obligation to the policyholder is to cover the policyholder's liability "in full" up to the policy limits. It is irrelevant that only part of the asbestos related disease developed during any single policy period or during a period in which the manufacturer had no insurance. . . . the policyholder is covered (up to the policy limits) for the full extent of its liability and need not pay a pro rata share.

Armstrong World Industries, Inc. v. Aetna Casualty & Surety Co., 45 Cal.App.4th 1, 57 (1996).

CONCLUSION

Depending on the particular jurisdiction in which it files suit, Gasco's prospects of recovering from its insurers appear to be good -- assuming that it can establish that property damage began or continued during a period in which it had insurance coverage in place. Because of the long term nature of such contamination and the tendency of remedial investigations to focus on the existing nature and extent of contamination, current managers and operators may overlook one of the most obvious sources of payment for remediation costs -- the company's liability insurers from the 1960's and 1970's. The Gasco scenario demonstrates that such an oversight could be a very costly mistake.

Environmental Regulation and Litigation

Engineers, historians, lawyers and scientists: Environmental Litigation and Industrial Archeology

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ABSTRACT

Environmental litigation has evolved into a complex undertaking. Defending or pursuing an environmental claim now requires a substantial investment in engineering, scientific, historical and legal research. Moreover, the lines of evidence that may be developed may involve highly non-traditional juxtapositions of disciplines. For example, a claim that oil field operations have polluted groundwater with salt might require the defense to prove that groundwater in that particular area was historically salty. Developing such a case might include locating historical documents containing specific statements regarding groundwater salinity or historical water sources, interpreting cable tool drillers logs and old electric logs and showing that local groundwater was too salty for use as boiler water in early drilling and production operations. Likewise, pursuing a liability claim against a PRP might require careful dissection of industrial processes conducted by the PRP with the goal of using the suite of released environmental contaminants as a fingerprint of that PRPs operation. Associating that suite of released contaminants with a stratigraphic horizon from the time window in which that potential PRP operated is powerful evidence. As can be readily appreciated, modern environmental litigation requires a team approach involving, engineers, historians, lawyers and scientists. These team members must develop a multi-disciplinary approach to the litigation. Legal strategies and approaches must live within the confines of engineering, historical and scientific possibilities. Engineers, historians and scientists must focus on making contributions which directly support the legal strategies being pursued.

ENVIRONMENTAL LEGAL PRACTICE

Environmental legal practice is complex and inherently multidisciplinary. Three main practice areas comprise the bulk of environmental legal practice: Environmental litigation, administrative - regulatory practice and transactional environmental practice. Each of these areas requires skillful application of the services of small armies of technical experts.

Environmental litigation activities focus on common law claims for damages to property and human health and life (toxic tort), natural resource damage claims, enforcement actions by state and federal regulatory agencies, indemnity and other contractual provisions allocating environmental responsibility and private and public claims under CERCLA, RCRA and other statutory provisions for remediation and cost recovery related to contaminated processing, manufacturing, pipeline, storage, disposal and other facilities. Because of the potential for class actions, this area of environmental legal practice can involve extremely large financial risk.

Administrative - Regulatory environmental practice involves interpretation and application of the various federal, state and local environmental statutes and their associated regulatory requirements. Aspects of this practice include representing clients in negotiations before administrative agencies, determining the applicability of regulatory requirements to a client's particular facilities or activities, advising clients on how to alter their activities to avoid costly or burdensome regulatory requirements, assisting clients in pro-actively affecting legislative enactments and rulemaking which may impact their activities, working with new or expanding facilities to identify applicable environmental permitting requirements or to renew, modify or avoid permits, assisting clients in the preparing for and conducting of environmental audits and implementing of related corrective action, and advising clients on the management and remediation of existing contamination. This area of environmental practice has become increasingly complex as new laws and regulations take effect. Moreover, because of its complexity, this area of law can be a "barrier to entry" to the marketplace for new businesses and new facilities of established businesses.

Transactional environmental practice supports the ongoing business activities of its clients by negotiating and drafting agreements allocating environmental risks in connection with leases, purchases and sales of real property, equipment, facilities and business entities and by providing advice and counseling on pre-transaction activities such as due diligence and environmental assessment, and post-transaction activities such as remediation of contamination and correction of non-compliance and deficiencies. Transactional environmental practice also involves representing clients in negotiating and drafting environmental service contracts, access agreements, and

contracts related to the treatment, storage, disposal, handling, transportation, or remediation of wastes and hazardous substances. This area of environmental practice endeavors to allow enterprises to conduct their businesses at minimum current cost and exposure to future liability.

EXPERT ROLES IN ENVIRONMENTAL LEGAL PRACTICE

What is an expert? Although it is certainly possible to describe the role of an expert differently, the definition provided in the Federal Rules of Evidence is an excellent place to start,

> If scientific, technical, or other specialized knowledge will assist the trier of fact to understand the evidence or to determine a fact in issue, a witness qualified as an expert by knowledge, skill, experience, training, or education, may testify thereto in the form of an opinion or otherwise. (Evid. Code §720; FRE 702).

What do experts do in environmental legal practice? Experts bring specialized knowledge and capabilities that assist the pursuit of clients' goals. In litigation, for example, experts can be used to more effectively pursue discovery, develop litigation themes, enhance case presentation and aid in the development of examination outlines for opposing experts. In administrative-regulatory practice experts can be used to identify and justify more cost effective compliance technologies and systems or develop position papers in support of a client's goals in the development of new laws and regulations. In transactional practice experts can provide the technical insights needed to avoid future liability or provide insights concerning costs of benefits of various waste management technologies.

How do experts' roles vary with environmental practice area? The bright line differences between experts working with counsel in purely administrative-regulatory or transactional practice from those working in litigation flow from the nature of the discovery process and the possible eventual requirement that expert testimony will be given at deposition and/or trial. In litigation practice it is very important to closely monitor all information provided to testifying experts. It is also critical to monitor, limit and control interactions among experts. Avoiding conflicts of interest is important in all environmental practice areas, but conflicts can be especially troubling in litigation or adversarial administrative-regulatory matters. Previously published opinions are also of greater significance in litigation practice. An expert who expressed opinions earlier publications or testimony in other matters which contradict opinions put forward in the matter at hand is probably not a liability in

transactional practice, but would be a severe liability in any adversarial matter.

EXPERTS MUST BE COMPETENT, CREDIBLE AND CLEAR

It is an imperfect world, but testifying experts need to be "good scouts" who communicate clearly. The ideal expert would, regardless of environmental practice area, be independent, competent, honest, trustworthy, easy to understand and persuasive. In litigation practice, these qualities have an acutely heightened significance. Testifying experts must be able to project their competence and honesty to the jury. Having degrees from prestigious institutions, meaningful honors, memberships in professional associations, a substantial publication record, a position of respect and a healthy head of flowing white hair may help. Being straightforward, positive, clear, consistent, unambiguous, sympathetic and understandable to the layman will help.

The jury must be able to both understand and believe the testimony given by an expert. Testifying, for example, "There is no definite proof of exposure." is a good deal less convincing than testifying "There is no way that the people living here could be exposed to any 'methyl-ethyl-death' in their soil." Testimony at trial or deposition is not a science lecture. People who say unintelligible things clearly or who can't enunciate a noun or a verb without immediately accompanying it with an adjective or an adverb sound like fools who are hiding the truth. If you don't believe this, consider how comics often make fun of politicians. When saying something unintelligible, it would be better if the expert mumbled and had a heavy accent; no one could understand the answer, and the expert would sound more impressive. Lastly, testifying experts must be cool under fire. Opposing counsel is certain to have prepared carefully, be advised by a panel of experts, and is, more likely than not, an expert at asking questions that are difficult or annoying to answer.

EXPERTS MUST WORK WELL IN A TEAM SETTING

Environmental litigation is costly. As environmental litigation has become more complex, the number and types of experts required to defend or pursue claims has increased. It is not uncommon to have six to ten technical experts (sometimes more) working full time on various tasks. These technical experts may be supported by others within their own organizations, and will be coordinated by attorneys and other professionals. Clearly, this level of activity represents a substantial cost to the client. A full day of effort by such a team of legal and technical talent could easily cost a client $15M to $20M (plus expenses). Legal and technical defense costs for a single

client in an Oklahoma oil field pollution case exceeded $900M. The median financial downside (both judgments and settlements) for a client defending a large oil field environmental action is, based on fifteen significant cases tracked by Gardere & Wynne, approximately $2.8MM (see Fig. 1 for a more detailed look at these statistics). Under any circumstance of cost and risk it is only reasonable and proper that a client expect and receive value. Certainly, in an environment of high costs and potentially high stakes, clients will closely watch how efficiently and effectively technical experts do their jobs.

To be effective and efficient, experts need to work as a team with legal counsel. The client may need to accept that the team is costly, but the client will never accept a group of technical experts who are uncoordinated, unmanageable, egotistical, internally conflicted, collectively incomprehensible and difficult schedule. The responsibility for management of the team is with counsel. Counsel must assemble and retain the technical team early in the litigation. Indeed, counsel may have a core team of technical experts retained as a "rapid reaction force" to handle technical issues until a formal technical expert team is formed for the purpose of a particular litigation. To run efficiently, the technical team must, as soon as possible, become familiar with the issues involved in the litigation and the other members of the litigation team, understand the long term strategic goals of the litigation and, if appropriate, visit the site(s) involved. Counsel must clearly define and explain the general assignment of each member of the technical team to that team member. Working with counsel, each member of the technical team should produce specific short-term work plan(s). As with any project plan, these work plans should include a brief description of each task (including its contribution to the overall litigation strategy), the actions that well be taken to accomplish the task, when those actions are anticipated to begin and end, the resources (human and financial) that will be required to accomplish each task, a description of the work product that each task will produce, the date on which it is anticipated that work product will be available. Although it may be necessary for counsel to prepare a document describing the interrelationships of all expert work products, individual experts should not specify these relationships in their work plans.

It is important for all technical experts to maintain regular communication with counsel. In litigation it sometimes seems that crises and changes in direction and timing occur daily. To the extent that these changes individually and cumulatively impact the timing, nature or extent of the technical experts' tasks counsel should communicate these changes promptly. The communication burden, however, is not entirely counsel's. Each member of the technical team should establish specific (named individuals) communication links with counsel's office and communicate regularly. Typically, this individual will be the person assigned by counsel as the information "gatekeeper" and will be responsible for coordination and management

of the technical team. Often the press of issues in a litigation may sweep away the best of counsel's and counsel's staff's intentions to communicate changes impacting an expert's work. Redundant communication is reliable communication. A hallmark of organizations involved in high stakes and high risk activities is constant and redundant communication and coordination. Consider, for example, launching and recovering aircraft from an aircraft carrier. If counsel doesn't call you, call them.

Counsel must clearly communicate and establish administrative procedures and contractual requirements with each expert when the expert team is formed. The sensitive issues of billing rate, expected level of detail and justification in the expert's billing, timeliness of fee payments and alternative dispute resolution must be discussed, understood, established and enforced early. Each expert must clearly understand that the information gained during the litigation is confidential; leaks are intolerable. Each expert must understand that all communications with other team members must be approved by counsel. The conditions under which subcontractors may work on behalf of any expert must be formally resolved. If applicable, special considerations concerning insurance against general liability and errors and omissions should be established.

PLANNING THE WORK AND WORKING THE PLAN

Below, is a generalized account of an oil field pollution given to illustrate the construction of a technical defense and the formation and operation of a technical expert team.

A formal complaint has been received. Your client, a large multinational corporation engaged in petroleum exploration and production has just been served notice that it is being sued by a group of plaintiffs who allege that petroleum extraction operations conducted by your client has injured the surface of their land, the quality of their groundwater and, consequently, the value of their property and their health. The plaintiffs present the usual list of charges: Negligence, trespass, nuisance, inherently dangerous activity and abnormally dangerous activity. The plaintiffs are requesting many types of relief: compensation for the diminished value of their property, compensation for their personal injuries, compensation for their emotional distress, compensation for the loss of use and enjoyment of their property, remediation of the conditions which produced the claimed environmental degradation, injunctive relief against further contamination, funding for medical and environmental monitoring, and punitive damages on the grounds that your client "...knew or recklessly disregarded that their conduct was dangerous ... did so heedlessly and recklessly, without regard to the consequences, and without regard to the rights and safety of

others...". It is small comfort that your client is not the sole defendant. That list is long as well (a fact that may create other heartaches). Your client sold the accused production operations over thirty years ago.

The strategic technical defenses of this case will depend on the chronology of events that took place and to some degree on the scientific underpinnings of the plaintiffs theories of causation. Below is a non-exhaustive strategic technical defense outline:

- The claimed damages do not or could not exist
  - The causation claimed by the plaintiffs cannot or is not supported by science
  - The damages claimed by the plaintiffs are false or misleading
  - There is are alternative explanations for the claimed damages

- Our client's activities did not or could not result in the claimed damages
  - The causation claimed by the plaintiffs is not scientifically possible
  - The causation claimed by the plaintiffs is possible, but would have occurred after our client sold its interests
  - There are alternative explanations for the claimed causations

- Even if our client's activities were responsible for the claimed damages our client is no longer legally responsible or, at least, the plaintiffs are at least partially to blame for their situation
  - The damages claimed happened in the past and recovery by the plaintiffs is precluded by a statute(s) of repose
  - The plaintiffs were aware of the damage before they purchased this land, and therefore moved to the nuisance

- Even if our client's activities were responsible for the claimed damages our client was not irresponsible or reckless
  - Our client operated within the regulatory guidelines applicable during the period they operated at this location
  - Our client used technology typically employed in such operations during the period they operated at this location
  - Our client fixed problems with the operation at this location as they became aware of them

It is now time to form and organize the expert team. Although this outline could be used to identify the the primary functional elements of an expert team, it is probably better to conduct additional investigation prior to identifying specific experts and expertise. This is because information developed may reveal either the need for one or more of the following: unanticipated specific expertise, a substantially expanded scope of inquiry, unanticipated conflicts of interest, etc. Basic information concerning oilfield operations at this location can generally be obtained from the client's archives. How many wells did the client operate in the area? When were

they drilled and completed? How were the wells and surface equipment maintained? When, were the wells sold? Are there parties not now named in the lawsuit who participated in the drilling and completion of the wells and construction of any surface facilities? Much of this document work will be useful as discovery progresses, and will certainly aid in preparation of an answer to the plaintiffs' complaint. In addition to the document work contemplated above, however, it may be adviseable to conduct an on-ground investigation (from public access) in the area of the lawsuit. Are there parties not now named in the lawsuit who are currently conducting operations in the area which might be sources of contamination? Lastly, the process of identifying and interviewing current and past employees who worked in the operation subject to the lawsuit should be initiated at this time. There are many ways to conduct these tasks, but, typically, the team responsible for their physical execution involves attorneys, paralegals, private investitigators and technical experts.

Technical review of the client's documents may require a geologist, a petroleum engineer, a reservoir engineer, and/or , possibly, other technical specialists. Although it may ultimately be necessary to name an outside consultant to testify about these documents, it may be more cost effective to obtain consulting technical specialists from the client's in-house resources.

Since the plaintiff's allege groundwater contamination, drafting an answer to the plaintiffs' petition will require a hydrogeologist. A soil scientist is required to address the plaintiffs' claims of soil damage. The timing of events is critical in this case with respect to when the damages took place in relationship to your client's tenure at the site. A very cost effective way to examine this aspect of the case is to obtain available aerial photography for the location and have it reviewed by a photogrammitrist. Many oilfield lawsuits involve fields which were initially developed during the first two decades of this century. Because of this, it may be advantageous to name a professional historian who specializes in oil industry history to the technical expert team. Knowing, for example, that pressure cementing did not become common practice until the late 1920s, that early surface pipe was sealed in the wellbore by wrapping a leather sack filled with linseed (which swelled as it became saturated with water) around the base of the pipe, that early oil well drilling was conducted with steam powered rigs (which needed large quantities of fresh water to operate) or that wells were stimulated by "shooting" them with nitroglycerine until the 1950s (when hydraulic fracturing was commercialized) may seem esoteric to a modern petroleum engineer, but is significant to experts working on a lawsuit involving an oilfield which reached peak production in 1919.

The medical and personal injury claims put forward by the plaintiffs are certainly significant; one or more medical experts (e.g. an environmental toxicologist, a medical doctor, etc.) will be required on the expert team. It may also be desireable

to retain an expert in environmental risk assessment to evaluate the source - pathway - receptor theory put forward by the plaintiffs.

The team assembled is diverse, and includes attorneys, paralegals, a private investigator, the client's archivist, a photogrammitrist, a soil scientist, a hydrogeologist, a medical doctor, an historian, a petroleum engineer, a geologist, a risk assessor, a toxicologist and a reservoir engineer.

Specific individuals must now be selected and retained. Once the expertise required has been identified, it will, of course, be necessary to identify specific individuals to fill these roles. A discussion of identifying and selecting individual experts is beyond the scope of this paper. However, this phase of the formation of the expert team is complicated by legal, human, and practical factors. Experts may have conflicts of interest, scheduling difficulties or personality conflicts with other team members in addition to getting sick, dying occasionally and being otherwise difficult to work with.

The experts must now be built into a team. After the expert team has been identified and retained, the next step will be to schedule an experts' orientation and brainstorming meeting. This meeting will have several purposes. At this meeting, counsel can efficiently orient the experts to the case, the current theory of strategic technical defense and the case calendar. The experts can help firm up the strategic technical defense and develop a work plan directed toward achieving the goals of the strategic technical defense. Lastly, this meeting will allow the experts to meet and interact with one another, counsel and counsel's staff. It is important to quietly observe these interactions to identify "problem" experts before they become disruptive to the smooth operation of the expert tem. This meeting will be difficult to organize and expensive to conduct. It is, therefore, imperative, that it be very carefully planned and executed.

It is important that you challange the assembled experts to really "get out of the box" at this meeting. If the experts have been well chosen, they well respond to this challange and may produce novel technical defense strategies and tactics. For example, in an oilfield groundwater pollution case in the early 1990s, an in-house geochemist, familiar with hydrocarbon analysis of fluid inclusions and radiometric dating met an Quaternary geologist who was intimately familiar with the geology of terrace gravels in the lawsuit area. Between them, they determined that the phreatic carbonate cemented zones in the terrace gravels could be analyzed for their content of hydrocarbon gases by fluid inclusion analysis. The time of trapping could be determined by obtaining a ^{14}C date of the carbonate cement and backed up by the stratigraphic age of the terrace gravel. This produced a line of evidence, based on hard data, that thermogenic hydrocarbons had been present in shallow groundwater in the lawsuit area up to 30,000 YBP.

Ultimately, the work product of this meeting will be a work activity plan designed to build lines of evidence which support the goals of the strategic technical defense.

The expert team will play a significant role in the discovery process. Appropriate members of the expert team will review the client's documents and documents produced by the plaintiffs in their efforts in support of the strategic technical defense. Any field investigations will be conducted by members of the expert team. The expert team will aid in drafting discovery requests made of the plaintiffs. Opinions given by opposing experts in the current case as well as relevant opinions expressed in the literature or in prior testimony will be critically examined by the expert team. If opposing experts will be deposed, members of the expert team will be involved in drafting deposition outlines and specific questions to be asked at the deposition. Members of the expert team identified as testifying experts may be deposed by the plaintiffs. Those individuals will work especially hard in preparing to be questioned concerning their opinions and the information upon which their opinions are based.

The expert team will be very involved in trial preparation. The experts may help develop an outline of their direct testimony, design cross-examination outlines for opposing experts and continue to refine their opinions. The experts will identify exhibits to be used at trial, and will design (and sometimes produce) visual aids (graphical aids, videos, animations, etc.)

At trial, the testifying experts, of course, will testify. The expert team may be called upon to evaluate testimony given by opposing experts to help modify cross-examination outlines and tactics. Throughout the trial, counsel will rely on the expert team to explain technical concepts, field technical questions and act as back-up sounding boards for testifying experts.

During the appeal (if any), the expert team may be called upon to help in constructing technical aspects of briefings. In general, however, once judgment has been rendered in the trial court, the experts can go to a low level of alert.

SUMMARY

A substantial investment in engineering, scientific, historical and legal research is required to pursue an environmental claim. As a consequence, the technical experts must be carefully and creatively managed as a team. Expert team members must develop a multi-disciplinary approach to the litigation, and be open to working and thinking synergistically. Legal strategies and approaches must live within the confines of engineering, historical and scientific possibilities. Technical experts make contributions which directly support the legal strategies being pursued.

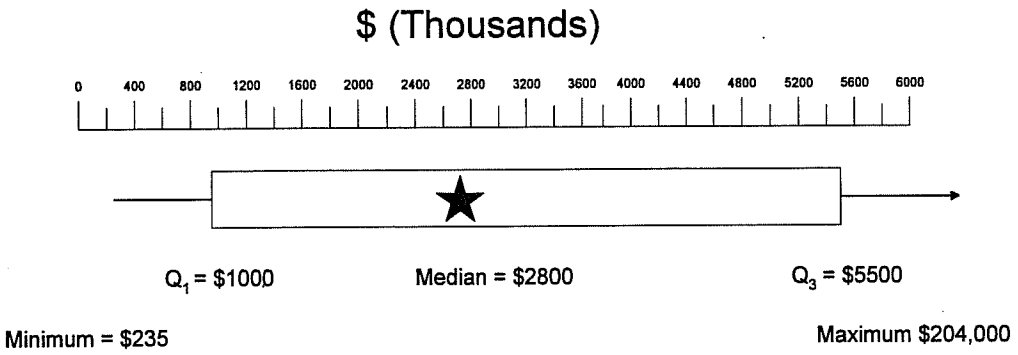

Figure 1. Judgments and Settlements in Fifteen Significant Cases Involving Major Exploration and Production Companies and Large Independents Monitored by Gardere & Wynne, L.L.P. from 1986 to 1996.

Litigating with Experts:

Management and Use of Technical Expertise

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This paper is intended to be a practical guide to the efficient and effective use of expert witnesses in complex litigation. This paper focuses on developing and maintaining the relationship between lawyers and expert, so that the expert's contribution to the case is maximized. An expert's mind is a terrible thing to waste.

I. INTRODUCTION

The notion of the simple law suit may be fading into the dusty recesses of yesterday's law practice, along with the old volumes of case reporters that contain the short, concise opinions that resolved those simple suits in a relatively predictable and efficient way. For not only has the number of suits increased exponentially over the past several years, but the complexity of each suit has increased as well.

Suits in every area of practice have followed this pattern, but suits concerning claims for environmental damage have become among the most complex. The use of more sophisticated terminology to describe traditional concepts and the increased scope of the claims alleged indicate the degree of significance attached to environmental suits. For instance, what used to be referred to simply as a property damage case is now described as a groundwater, surface water, or soil pollution case, and a nuisance is now referred to as a point source. Claims that once were brought only by the owner whose property had been directly affected by the alleged tort are now being brought by anyone who can allege even a tangential connection to the property, and even by citizens who are acting as private attorneys general and have no connection with the property at all. Damages that once were limited to diminution in property value now are likely to include recovery on a host of personal injury claims, both real and perceived, claims for abatement of the alleged nuisance and restoration of the allegedly damaged resource, and the most unpredictable category of punitive damages. In short, the game has changed, the rules have been made more liberal, and the exposure has increased dramatically.

"Complex litigation" implies litigation involving a warehouse of documents and a crowd of people. That crowd undoubtedly will include a team of attorneys, outside and perhaps in-house, a long list of potential fact witnesses, various levels of support staff, and consulting and testifying expert witnesses. One practical definition of "complex litigation" may in fact be the necessary participation of myriad expert witnesses.

Complex litigation, particularly complex environmental litigation, requires the use of expert witnesses from many disciplines. To many litigators, the least palatable part of preparing their case is working with their expert witnesses. This uncomfortable association may be caused by a clash in egos or the litigator's lack of time, interest, or ability to understand the expert's language. The end result, invariably, is a litigator frustrated because his expert did not do what the litigator wanted and an expert frustrated because he never really knew what was expected of him.

The aggressive use of expert witnesses is not without its detractors. Clients, even larger corporate clients, often do not readily embrace such a strategy for two principal reasons: a reluctance to gather information about the nature of the problem and an aversion to the cost associated with such an approach. There is still a school of thought, though obsolescent, that clings to the idea that ignorance is bliss. In other words, those who subscribe to that view think data gathering by experts can only dig a deeper hole of liability and exposure, making it preferable not to know. Of course, data should not be gathered without a specific purpose in mind, and such decisions should be made judiciously, but in these environmental times, ignorance is anything but bliss. Not finding out the true nature and scope of contamination will not afford any protection based on ignorance. Simply by discovering that a problem exists, a plaintiff has psychologically carried his burden. Defendants who fail to investigate for fear of the unknown also fail to avail themselves of opportunities and strategies that can be discovered only through expert investigation.

The objection to cost is common but understandable. No one likes to spend money defending law suits. Clients are loathe to spend any more than absolutely necessary. They have had to accept having to pay lawyers a lot of money, but they do not always understand and appreciate the need for experts. If finally convinced of the need for one expert, they certainly do not understand the need for more than one. Nor do they understand why an expert is needed for more than deposition and trial testimony. After all, if they are experts, shouldn't they already know it all?

Environmental cases require experts. Usually, they require many experts, and proper preparation requires much of their time. A lot of time from a lot of experts will, unavoidably, cost a lot of money. Clients must be shown that the aggressive use of experts is a justified and necessary cost of defense.

Environmental catastrophes like the Exxon Valdez oil spill and the Union Carbide disaster in Bhopal, India are not really as susceptible to the objection of cost because the significance of the event indisputably justifies the expenditure of great sums of money, although even in those cases, the concepts of efficiency and organization still apply.

More important to my message and of more practical use to you are the innumerable cases that are not necessarily described as cataclysmic events and yet are of great importance to the affected population. These cases are much more insidious because clients do not feel automatically compelled to prepare their defense as they might if Congress were holding special hearings on the subject of the suit. It is in these cases that the need for the appropriate experts and the timely and efficient use of those experts must be emphasized.

The following outline contains no citations and is not meant to be a survey of case law concerning the use of expert witnesses. It is, instead, a practical guide, the goal of which is to emphasize the importance of expert witnesses in complex litigation. It is of general application but is prompted by my experience in handling environmental litigation.

II. GUIDE TO USING EXPERT WITNESSES

A. When Should the Process Begin?

1. The process of identifying and selecting experts should begin immediately upon receipt of the complaint. You should identify areas of expertise potentially required based on the nature of the claims made in the complaint. Not all areas will be readily discernible and may require development and clarification through amendments to the complaint and discovery.

2. Once general areas of experts have been identified, you should begin identifying expert witness candidates for those areas. Not all areas should be acted upon simultaneously. You should prioritize according to the relative importance of each area.

   Why so soon? Why not wait a few months and let the plaintiff prosecute his claim?

   a. This might be the most common and most aggravating mistake outside counsel can make. It is symptomatic of an inadequately designed, if not altogether non-existent defense strategy. Procrastination leads to rushed, poorly researched choices of experts. An even greater risk is that the expert of choice will not be available. In environmental cases, the supply of particular kinds of experts, as well as the individuals themselves, is still small, and the demand is great. If you wait too long to find the right expert, it is likely that the plaintiff or a co-defendant will have already retained him, or the expert's schedule will not permit the sudden onslaught of a new case with little time to prepare.

b. In most environmental cases, the existence of some damage of some kind caused by somebody will be unquestioned. Psychologically, if not in reality, a plaintiff will have carried his burden simply by claiming damage has occurred. The real battle will be in determining what kind of damage, caused by whom, and when. Consequently, it is much more efficient to involve the experts from the outset of the case.

c. Knowledge is power, and the only way to become knowledgeable is by using your experts to begin the process of gathering and analyzing data and formulating theories based on that data. Equipped with that knowledge early in a case enables you to exercise more informed strategies with respect to conducting discovery, filing cross-claims and dispositive motions, narrowing the claims, negotiating with the plaintiff and other co-defendants, if any, and the general advantage of having superiority over those with less knowledge. Decisions based on more information are always superior to those based on less. Always make sure you are the party with more information.

III. HOW SHOULD THE PROCESS BEGIN?

A. Start shopping upon receipt of the complaint, but know where to look.

1. Professional Associations -
Organizations like the American Petroleum Institute and the Society of Petroleum Engineers are great resources.

2. Treatises, Texts, Articles -
Consult your library or computer for names of authors who have written on the subject with which you are concerned.

3. Colleges and Universities -
Check locally first if there is a regional advantage.

4. Research Organizations -

These are often associated with particular departments of colleges and universities.

5. Consulting Firms -
More often than not, college and university professors have consulting businesses on the side. Some have actually decided to go into consulting full time.

6. Other litigation with Similar Claims -
Check around for other suits that have similar claims or facts, especially if your opposing counsel is involved. Find out who the experts are in those cases. If they are good, you may save some money on the learning curve; if they are not good, you can delete them from your list of candidates.

7. Expert Database -
Perhaps your firm or your client maintains an expert witness database developed from past experiences. If so, don't forget to consult it. If not, conduct an informal survey of other attorneys in your firm and of your client with the same objective (and use this opportunity to start your own database).

8. Seminars -
Consult programs from any seminars that may have been given on the subject of your case and identify any consultants who may have been advertised as experts in particular areas.

9. Expert Witness Networks -
When all else fails, there are directories provided through expert witness locating services that identify experts for every conceivable area of expertise. At the very least, these services can put you in contact with someone with general knowledge.

B. Request resumes from the most promising candidates. Look for litigation experience, professional credentials, and published articles on the subject of the suit.

C. Interview the candidates with the most impressive resumes. After all, this is just like any other job. Involve the client to the extent

desirable or necessary. A client's input in the selection process can defuse later disagreements or dissatisfaction.

IV. WHAT SHOULD YOU LOOK FOR?

A. The goal of the search is to find an expert who is sufficiently knowledgeable in his area of expertise and is capable of communicating that knowledge to others.

1. The assumption is that each party will match expert for expert in every area. Since the experts will consequently be compared to each other, you should make sure there is no doubt that your expert is more knowledgeable. However, even if he is in fact more knowledgeable, that advantage is lost if he is unable to communicate his superior knowledge.

2. Identifying a candidate and reviewing his resume are for the purpose of assessing knowledge and expertise. Interviewing a candidate is for the purpose of assessing his communication skills and appearance.

B. The expert should not only be knowledgeable about the technical and scientific aspects of his area, but he should also be knowledgeable about law suits, litigation strategy, and the ways in which his talents are to be used.

1. Investigate his litigation experience. An expert without experience in testifying under cross-examination can be very risky.

2. Check his litigation references. Do not hesitate to talk to other attorneys or clients for whom the expert has worked. This may help identify unattractive traits about certain experts that are not readily discernible, so that you steer clear of those candidates; and it may help you learn how effective others are. If possible, obtain samples of testimony from transcripts of past depositions and trials.

C. Determine his support capabilities. If a lot of field work is to be done, this could be an important factor. If you can provide him with field personnel, and he is comfortable working with them, this need not be as much of a concern. There is even some potential strategic benefit in conducting your field work through a consulting

expert and developing preliminary conclusions from that work before involving your testifying expert, in that you can keep that work confidential for a longer period of time.

D. Although cost is an important consideration, don't make the mistake of choosing an inferior expert simply to save money. As with most things, you get what you pay for. Even expensive experts can be well worth the investment when used efficiently. At the same time, be aware of the market rate and don't be afraid to negotiate what you consider to be a fair deal.

E. Make sure the candidate's schedule will permit the degree of commitment you require. If you retain a college professor, make sure his teaching schedule will not interfere with his responsibilities in the case.

F. The expert simply must be able to communicate effectively. Some grooming will always be necessary, but make sure you choose an expert who has the basic ability to translate his scientific jargon into language that would be understandable to a jury. Chances are that if the candidate is unable to communicate with you, he will be unable to communicate with the judge and jury.

V. WHAT SHOULD YOU DO AFTER YOU HAVE CHOSEN YOUR EXPERT

A. Determine what kind of contractual arrangement is required and how bills are to be submitted and paid. Confirming these details at the beginning can help avoid a lot of unnecessary distraction later when you and the expert can least afford.

B. After the general terms of the arrangement have been agreed upon, but before any work is performed, you should meet with your expert and discuss the long-term strategy and general assignment. Then, the expert should be required to break down his long-term assignment into short-term, manageable workplans. Each workplan can then be discussed and approved or rejected as submitted. This approach helps keep you, the expert, and the client focused on the purpose of the expert's work. Since timing in an expert investigation is critical and certain phases of an investigation may not be necessary if certain claims are modified or deleted altogether, short-term workplans can also provide tactical and economic benefits.

C. The expert should be integrated into the defense team immediately. He should visit the site and become generally familiar with the project as soon as possible. Regular organizational meetings should be held in order to assure maintenance of focus, confirm work assignments, and discuss problems that may have developed.

VI. HOW SHOULD YOU ORGANIZE YOUR EXPERT DURING THE CASE?

A. It is important that you develop protocols for your expert. (See Exhibit 1). They help prevent mistakes from being made and provide a structure that makes experts feel more comfortable. They should be manageable and practically functional.

1. If possible, reach an agreement with opposing counsel concerning gaining access to the property for observation, testing, etc. (See Exhibit 2). If opposing counsel is not amenable, obtain an order from the court assuring access for your expert.

2. Establish a protocol for communicating with outside counsel. In complex cases, because there is typically so many people involved, it is all too easy for several lines of communication to develop between various parties, especially involving the expert witnesses. Allowing multiple lines of communication to exist is unavoidably confusing for everyone. The experts should communicate with you only to make reports and receive instructions. You can then discuss issues relating to the use of the experts with the client. Never let the experts communicate with anyone else, not even for arranging site visits, etc.

3. The experts should never reduce any of their work to writing a draft report until they are sufficiently comfortable with their preliminary conclusions and they have been specifically instructed by you to do so. Nothing looks worse at an expert's deposition than conflicting reports. Usually, the conflict is the result of preparing an earlier report based more on speculation than fact. Even the later report is factually more accurate, the expert will spend most of his time trying to explain why his earlier report is wrong.

B. Develop an overall defensive strategy for the expert and make short-term assignments designed to implement that strategy.

1. Just as lawyers must take the time to understand the expert's language, so, too, must the experts be made to understand the nature of the litigation and the objectives of the defense. In fact, this point cannot be emphasized enough. Never assume the experts know what your strategy is or how you plan to use them to carry out that strategy.

2. Communication is key. You should schedule regular meetings with your experts to assure completion of assigned tasks and discuss what should be done next. (See Exhibit 3). Do not isolate your experts from each other. Emphasize a team approach. It is beneficial for an expert to know the objectives of the other experts on the team. this kind of coordination will minimize the potential for experts working at cross purposes. If there are several experts involved, you should supplement the regular group meetings with individual meetings.

3. Prepare and utilize written task lists to make sure everyone understands the jobs to be done. (See Exhibit 4). Instruct the experts to submit their recommended work in writing, along with cost and time estimates. Once these recommendations have been accepted, they should be converted into short-term workplans. (See Exhibit 5).

4. Monitor performance between meetings by assigning an associate or paralegal to make weekly calls to the experts.

C. Involve the experts in the discovery process. Not only have them participate in responding to discovery requests, but also involve them in the formulation of discovery requests served on the opposition. Without question, the experts should attend all depositions of other experts (i.e., discipline to discipline). Not only can they help you interrogate the plaintiffs' expert, but the exercise will also help prepare them for their own depositions. Generally, it will be sufficient simply to review the transcripts of depositions of fact witnesses.

D. Always make the plaintiffs' experts give their depositions first. After all, it is the plaintiff's suit. When it is time for your expert

to testify, both at deposition and at trial, make sure you have prepared him.

1. As stated above, always have your experts attend the depositions of the other experts. In advance, obtain a "wish list" of information your experts would like to have from the plaintiff's experts.

2. Have them practice using any exhibits or demonstrative aids they intend to use.

3. Have them rehearse giving responsive and communicative answers. Challenge their answers and opinions. Identify problems such as argumentativeness, loss of focus, narration, non-responsiveness, etc. If the deposition is to be videotaped, rehearse posture, facial expressions, voice projection and inflection, etc.

VI. CONCLUSION

The recommendations made in this outline are, in reality, all based on common sense. You are perhaps even assuming that these recommendations are already routinely followed in all cases. I can assure you they are not, and that failure is to the ultimate detriment of the defendant. Environmental cases are too complex and the financial exposure is too great not to follow the kind of detailed procedure for using experts that is outlined in this paper. The expert is the case in environmental litigation -- use him well.

EXHIBIT 1

DRAFT PROTOCOLS

DISCOVERY PRACTICE TEXT:

- Prepare a report with the expectation of having to disclose it.

PROTECTING YOUR EXPERT FROM DISCOVERY:

- Be even-handed in providing selected background materials. Provide good and bad documents in anticipation of discovery.

- Any reports, summaries or recommendations, etc. are to be stamped DRAFT until finalized with counsel.

  Any drafts, notes, investigative materials, or correspondence may be discoverable.

- Discourage annotation or highlighting of materials.

- Instruct experts not to record preliminary conclusions until the nature and scope of the testimony has crystallized.

- Discuss with experts in detail the content of any report before it is committed to writing.

EXPERT WORK NOTES:

- Telephone Log - commentary only as to opposition experts or plaintiffs' counsel.

- No written reports without prior approval from trial counsel

  - Except - Reports, work papers or data regularly maintained in course of business or investigation (i.e., field notes, tests, data generally).

- Bates-stamped-page-numbered records must be maintained in litigation documents reviewed or relied upon.

- Complete set of field notes maintained in a permanent notebook every day that expert is in the field.

- No talking to anyone other than XYZ Corp. counsel about the case:

  Except with specific authorization of XYZ Corp. counsel.

  Except other XYZ Corp. trial experts to extent necessary.

  DO NOT discuss opinions reached or strategies between disciplines or areas.

- Supply requested documents only to XYZ Corp. counsel, NEVER to lawyers on other side, and NEVER to other witnesses on our side, unless specifically instructed by XYZ's Corp. counsel to do so. Keep record of documents supplied or exchanged.

- No correspondence between experts, except data receipts and necessary transmittal letters.

MISCELLANEOUS:

SAMPLE CONTROLS - Uniform science to science; chain of custody control samples; storage and maintenance; data dissemination

TESTING REGIMEN AND PARAMETERS

INVESTIGATION ORDER - i.e., Engineering Review of Well Data;
EM Survey (On and Off Lease)
Off Lease Monitor Wells
Off Lease Engineering Review
Soil Samples
Surface Water Samples
Hand-Dug Well Samples
Monitor Wells

** Must be accessible on a priority basis - return callas as promptly as reasonably possible. **

EXHIBIT 2

(Date)

_____
_____
_____
_____

RE: ABC Corporation v. XYZ Corporation

Dear _____:

This letter constitutes notification to the plaintiffs that certain of _____ experts will be entering plaintiffs' property to conduct _____ during the hours between 8:00 a.m. through 5:00 p.m. on Monday, _____ through Friday _____. The following represents the property which will be entered, subject to unforeseen circumstances.

_____
_____
_____

Very truly yours,

_____

(Exhibit 2 Cont'd)

Name	Date	Property to Be Entered	Activity	Time In

EXHIBIT 3

ABC CORPORATION v. XYZ CORPORATION
1/1/99 Expert Meeting Outline

A. CASE STATUS REPORT

1. Procedural Developments and Scheduling
2. Fact Witness Deposition
3. Experts Deposition Schedules
4. Final Preparation for Plaintiffs' Expert Depositions
5. Final Preparation for Giving Expert Depositions

B. GENERAL AGENDA

1. Housekeeping
2. Plaintiffs' Pollution Abatement Plan

C. EXPERT STATUS REPORTS - BY SCIENCE

1. Petroleum Engineering
2. Reservoir Engineering
3. Waterflood Engineering
4. Geology
5. Hydrogeology
6. Soil Science/Agronomy
7. toxicology
8. Environmental Policies
9. Historical
10. Appraisal/Lane
11. Accounting/Economics
12. Remediation

D. DEMONSTRATIVE EXHIBITS

1. Exhibit Identification
2. Video Exhibit Task List
   a. Video Exhibits Status
   b. Hardcopy Exhibits

E. DEFENSES, STRATEGIES AND THEMES-OVERVIEW OF THE LAW

F. LEGAL (MISCELLANEOUS QUESTIONS, STATUS, ETC...)

G. CLEAN-UP/CONCLUSION

1. Additional Requests by Attorneys
2. Additional Requests by Experts

EXHIBIT 4

ABC Corporation v. XYZ Corporation

DAILY TASK LIST

Person	Completion Date	Task Description	Completed
EXP/ALL	03/04/99	Advise of specific areas of concern of possible testimony by 30(B)(6) designees. (117)	Y
EXP/ALL	03/05/99	Explain technical data and goals regarding each individual's testimony (list and prioritize) with outlines at meeting. This is coming in with outlines. (123)	Y
EXP/ALL	03/12/99	Provide outlines for plaintiffs expert depos (re: interrogatory, affidavits, etc.) (236)	Y
EXP/GEO	04/30/99	Provide strip logs samples to discuss at next meeting. (212)	Y
EXP/HYD	04/30/99	Map of useable groundwater (OCC) (286)	Y
EXP/HYD	04/30/99	Discuss EM maps for plaintiffs and adjacent tracts, problems. (406)	Y
EXP/ALL	05/07/99	Provide suggested outlines for plaintiffs expert depos by science/group (coming in slowly). (122)	Y

CONFIDENTIAL ATTORNEY WORK PRODUCT

EXHIBIT 5

PROPOSED WORKPLANS FOR
ABC CORPORATION v. XYZ CORPORATION

prepared for

by

(Date)

DRAFT - CONFIDENTIAL ATTORNEY WORK PRODUCT

WORKPLAN I

The goal of this workplan is to obtain initial field information in (specific location). Costs incurred to interpret the data and include it in previous data interpretations are included in the cost estimates per task.

The following tasks will be conducted as a part of this workplan:

Task 1:

Task 2:

Task 3:

Task 4: travel and per diem ($_____)

The field work for this workplan will take approximately _____ week(s) to complete, and analysis of the data will take approximately _____ week(s). Laboratory analysis will take _____ week(s). The total cost estimate to complete Workplan I is approximately $_____.

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(Date)

WORKPLAN II

The goal of Workplan II is to _____

_____

and complete additional minor tasks as requested.

Since the amount of work needed to accomplish this task cannot be estimated, nor can the number of minor tasks be determined, a cost per task cannot be given. Costs incurred for this task will be billed according to our normal fee rates. If any tasks appear too large to be included as part of this workplan, then a separate cost estimate will be submitted prior to any work being conducted on the task. Total cost for this workplan will not exceed $_____.

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(Date)

WORKPLAN _____*

The goal of Workplan _____ if to _____.
The following tasks will be accomplished as a part of this workplan.

Task 1:

Task 2:

Task 3:

Task 4: data analysis and graphics preparation ($_____).

Task 5: travel and per diem ($_____).

The field work for this workplan will take approximately _____ week(s) to complete, and analysis of the date will take approximately _____ week(s). Laboratory analysis will take approximately _____ week(s). The total cost estimate to complete Workplan ____ is approximately $_____.

* May prepare as many as needed. One per specific "workplan category" for groups of tasks to be completed.

DRAFT - CONFIDENTIAL ATTORNEY WORK PRODUCT
(Date)

Structuring and Negotiating

Risk Based Corrective Action Remedial Solutions

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Abstract:

Achieving a risk based corrective action (RBCA) remedial solution for a contaminated industrial site is often a highly desirable goal. This form of remedial solution is both cost effective and protective of human health and the environment. Despite the seemingly flawless logic of the RBCA approach, however, a successful RBCA remedial solution cannot be achieved without diligent and careful research, planning, negotiation and communication. To be successful, a RBCA remedial solution must be achievable given the scientific and engineering realities present at the site, comply with applicable federal, state and local environmental laws, and represent a consensus view of all parties involved. This is not as simple as it sounds. As desirable as it might be, is it reasonable to seek a RBCA remedial solution for a large industrial site situated on a sole source aquifer? What happens when, in an attempt to achieve a meaningful sitewide RBCA remedial solution, additional sampling and analysis reveals unanticipated RCRA concerns? Can a RBCA remedial solution be structured to serve the cost control needs of remediation funders and the liability control needs of facility managers? Lastly, as desirable as RBCA remedial solutions may be from technical and financial viewpoints, how will such solutions be viewed by special interest groups and public at large?

I. The Advantages of RBCA

In many circumstances the use of RBCA to determine appropriate site cleanup levels benefits both the party responsible for implementing the cleanup and those persons who are affected by the contamination. Traditional cleanups have focused on using "default" or "published" cleanup standards which are intended to be protective of the human health and environment for just about all situations. As such, traditional site cleanup levels employ a "one site fits all" approach which does little or nothing to assess the actual risks and evaluate appropriate solutions in response to those risks presented by contamination at the site. RBCA, on the other hand, requires that the actual risks presented by the contamination at a site be evaluated and solutions to address those risks be specifically tailored to site circumstances. Consequently, known risks are addressed by specific solutions individually developed to mitigate those risks.

Another advantage of RBCA is that it tends to result in an efficient use of resources. The RBCA approach seeks to only address appreciable or real risks rather than speculative risks that are not associated with the circumstances at the site. Accordingly, those risks that are present at the site can be addressed through application of resources. On the other hand, resources are conserved and not wasted on addressing issues that do not present problems for the parties affected by the contamination at a site. Because of it's efficient use of resources, RBCA often saves the responsible party money because the typical default remediation standards assume a residential use scenario. The residential use scenario assumes maximum exposure, such as actual contact with and ingestion of contaminated soils and waters. They also assume a long period of exposure. On the other hand, it is often plausible to propose an industrial or commercial use for a particular site which reduces the exposure to contaminants and thereby reduces the risk associated with contaminants found on the site.

Finally, RBCA encourages use of "natural" remediation techniques such as natural attenuation and biodegradation. Utilization of these natural remediation techniques can be justified based on risk analysis during the "remediation period" and substantiated through on site monitoring. Often, monitoring of the natural attenuation and bioremediation processes is much less costly than active remediation. Accordingly, RBCA's performance based remedial standards allows a responsible person to creatively, yet soundly, design a remedial solution that allows the flexibility to approach each site on an individual basis.

II. How RBCA Works

The overall goal of RBCA is to develop site specific target cleanup levels. These target cleanup levels are then used as a management tool to identify the appropriate remedial/response action for each site. Overall, the primary considerations of a RBCA analysis include: property use (*i.e.*, identification of contaminant receptors and exposure scenarios), contaminant characteristics (*i.e.*, hazard and toxicity), site specific soil and groundwater characteristics, institutional controls and engineering barriers used to control contaminant exposures.

These primary considerations are typically applied in a step wise manner that usually employs a tiered analysis. The ASTM model, which is rapidly gaining acceptance, employs these tiers. Each tier progressively establishes more site specific (and typically less conservative) target cleanup levels using more and more information about the site. Site conditions are then compared with the particular tier's target cleanup level to determine if further action is required. "Further action" is required if the site contaminant levels exceed the target cleanup level. Usually, further action consists of either site remediation or developing the next tier's target cleanup levels using more detailed site information. The steps of the RBCA process can be summarized as follows:

Initial site investigation and development of the site conceptual model - The initial site assessment focuses on acquiring data that is necessary for establishing the initial evaluation of risk to human health and the environment. The site investigation and development of the site conceptual model will include an evaluation of the contaminants present at the site with some analysis to determine the probable maximum concentration of each contaminant and the scope and extent of their presence at the site. Also, the location of the contaminants needs to be identified, both from a geographical and media context (*i.e.* where is the soil or groundwater contamination). Additionally, the site investigation should identify the potential receptors affected by the site contaminants. Typical receptors would be groundwater wells, utility lines (typical preferential pathways), buildings, groundwater, surface water, human use (on and off site) and environmental receptors (on and off site). Once the receptors are identified then the initial site assessment and analysis should evaluate the potential exposure scenarios by identifying the migration pathways for the contaminants. Migration pathways include ground and surface water migration over or through contaminated soils, vapors leaving the contaminated soil and groundwater, and other human and environmental receptor contacts with the contaminants. Finally, basic site physical properties such as hydrological conditions (groundwater flow direction, gradient and depth), current and future site uses, and any confining apparatus such as pavement or building coverings are identified and qualitatively evaluated for the site conceptual model.

Identification of chemicals of concern - Following creation of the site conceptual model through site investigation, assessment, and analysis, the target chemicals of concern can be identified. Typically, any chemical which is detected above background concentration is initially placed on the list of chemicals of concern through the Tier 1 analysis.

Identification of receptors through exposure pathways - Also using the information obtained in the site investigation and summarized on the site conceptual model, potential receptors, *i.e.*, the subjects that could be at risk based on the contaminants found at the site, are identified by determining whether or not there is a "complete exposure pathway" from the contaminant's location in the environmental media to the receptor. In other words, only those receptors that could actually be exposed to the contamination are considered for risk analysis. Consequently, in this step of the RBCA process, the sources of the contamination are evaluated in terms of "transport mechanisms." Those transport mechanisms are then linked with a potential exposure pathway and a particular receptor. For example, the transport mechanisms for soils include wind erosion and atmospheric dispersion (dust), contaminant volatilization and contaminant leaching to surface and groundwater. Transport mechanisms for contaminated groundwater include contaminant volatilization and migration to storm/surface waters and groundwater transport. Exposure pathways that may be identified with soil transport include soil ingestion, adsorption and inhalation of contaminant vapors emanating from the soils. Similarly, exposure pathways associated with groundwater include water use for drinking, adsorption and exposure through recreational activities, and contaminant vapors from the water. If it can be determined that there is a complete pathway between the contaminant source and a receptor, then that contaminant is next evaluated for it's toxicological effects on each receptor for which it is in contact.

Hazard characterization and creation of Tier 1 risk based screening levels - Using the complete exposure pathways identified in the preceding steps, hazard characterization is then accomplished by evaluating what is expected to be the reasonable exposures or daily chemical/contaminant intake for a receptor for using all exposure pathways. This dose exposure analysis is then compared to the toxicological information relating to chemical specific dose responses for humans and environmental receptors. Typically, chemical hazard characterization assumes reasonable maximum exposure parameters and evaluates those exposures in light of current toxicological information. The toxicologist then evaluates what the maximum dose or concentration of a chemical a particular receptor may be exposed to without incurring unreasonable risk. Typically, risk is considered unreasonable if it's carcinogenic slope factor is less that 10^{-6} or it's hazard index is less than 1. Upon completion of the chemical hazard evaluation a table is created that lists by chemical of concerns the risk based screening level (RBSL)

(or maximum dose) that is used in a Tier 1 evaluation and becomes the initial target cleanup goal. These constitute the "base line" cleanup objectives for the site. They are typically the most conservative targets because they assume that the receptor is exposed to the chemical concentration identified in the analysis.

Tier 1 evaluation - The Tier 1 evaluation compares the concentration of the contaminants detected at the site to the base line RBSL. If the contaminants at the facility are below the RBSL then the responsible person has the option of presenting a "no further action" alternative to the regulatory agency. On the other hand, if one or more chemicals of concern exceed the RBSLs then the responsible person must either remediate the site to achieve the RBSL for those chemicals that exceeded the base line level or proceed to develop more site specific target cleanup levels by using fate and transport modeling for the contaminants that exceed the RBSLs.

Creation of Tier 2 site specific target levels - Tier 2 analysis begins by establishing new site specific target levels (SSTLs) for those chemicals of concern that exceeded the Tier 1 RBSLs. Essentially, Tier 2 target cleanup levels are back calculated so that an acceptable concentration at the contaminant source is derived from the RBSL by applying dilution and attenuation factors (DAFs). The DAFs are developed using the site conceptual model and additional site specific information. Consequently, at this stage of the process, it may be necessary to do additional site analysis and investigation in order to get information that will establish soil attenuation factors, site specific hydrogeologic properties, engineering barriers and the potential for institutional controls such as deed and use restrictions for the site. A DAF is then calculated for each chemical of concern through the use of a numerical model based on site specific physical information. The SSTLs are established by multiplying the RBSL for a chemical of concern by it's DAF.

Models that are used to evaluate dispersion and attenuation of contaminants and calculate DAFs include: "See- soil" and AT-123D. The Tier 2 evaluation assumes the point of exposure is separate from the source. Accordingly, simple analytical models can be employed to determine the concentration level that may be left on site and still achieve the RBSL at the point the contaminant reaches the receptor.

Tier 2 evaluation - If the concentrations at the site are below the SSTL determined through the Tier 2 process, then the responsible person may submit a "no further action" proposal to the regulatory agency. If, however, one or more of the contaminants exceed the SSTL established for the site then the responsible person must either remediate the site until it achieves the SSTL or proceed to a more detailed site assessment.

Creation of Tier 3 target cleanup levels - In the Tier 3 process the actual contaminant concentration at the site is modeled to the specific point of exposure using fate and transport models and/or a probabilistic evaluation of the site contaminant concentrations. This evaluation allows for development of Tier 3 target levels, which then allow the responsible person to determine whether or not "no further action" is needed (the site contamination concentrations are below the Tier 3 SSTLs) or remediation must be undertaken to meet or exceed the Tier 3 action levels. Typically, no further upgrades or additional evaluation goes beyond the Tier 3 analysis in RBCA.

Remedial response selection is a part of each step of a tiered evaluation. Consequently, at the end of each tier analysis, the responsible person should determine the alternative remedial actions that may be taken in light of the site conditions, concentrations and target concentration cleanup levels that have been established. The ease or difficulty of achieving the remedial alternatives typically is the determining factor in whether or not the responsible person will proceed to the next step of the evaluation. A simple schematic drawing of the tiered RBCA decision making process is given in Figure 1.

III. Applicability of RBCA to Your Site

Beginning with the Superfund program under CERCLA and followed by publication of the ASTM Standard Guide for Risk Based Corrective Action Applied at Petroleum Relief Sites (E1739-95), the risk assessment approach to setting cleanup target levels is becoming more accepted. Indeed, because most state and federal environmental regulations have as their cleanup standard the overall goal of protecting "human health and the environment", RBCA's scientific analysis of specific site circumstances and risk should always satisfy the legal standards governing cleanup levels. EPA has acknowledged the RBCA process not only for the Superfund program, but also in it's recent Guidance on Soil Screening Levels (SSL) (1994) and with respect to it's proposed rules governing RCRA corrective actions. Consequently, the RBCA approach for setting cleanup standards at a contaminated site can be proposed for the following types of actions:

RCRA Corrective Actions
RCRA Closure Plans
Voluntary Site Cleanups
LUST Programs
CERCLA/Superfund Cleanups.

Many states have specifically authorized use of risk assessment for cleanups relating to leaking underground storage tanks and under their comparable

"Superfund"/hazardous site cleanup programs. However, even when specific authorization is not provided either by state statute or regulation, because most environmental statutes adopt the general goal of protecting the human health and the environment, it is appropriate for a responsible person to seek to negotiate for the adoption of a RBCA approach feeling confident that such an approach would be legally permissible under federal and state law. The primary difficulty in gaining approval of a RBCA approach is not legal authority, rather it is the lack of understanding concerning the RBCA process. This lack of understanding leads to the regulator's discomfort with, uncertainty and fear of public criticism. In approaching a regulator concerning a RBCA approach, examples of successful RBCA cleanup programs used in other states or within the same EPA region should be cited as a mechanism by which the regulatory agency can feel comfortable that the approach is appropriate because it has been successfully accomplished in the past. The more similar the contamination and site characteristics are, the more applicable and persuasive the precedent should be with the regulatory agency.

IV. How to Implement RBCA at Your Site

Implementing a successful RBCA cleanup requires the use of both legal and technical expertise. The utilization of this expertise usually leads to efficient and cost effective cleanup proposals for most sites that require more than the most minor response actions. In order to successfully implement RBCA, the technical expertise should include groundwater modeling and toxicology. Experts with these experiences should be initially consulted with regard to their overall impressions of the appropriateness and potential success of implementing RBCA at the site. Legal experts should be consulted concerning the methods and requirements needed in order to satisfy applicable laws governing remediation of the site. The legal expert can also assist with presentations to the environmental agency and negotiation of the remedial standards. The team should first identify whether the site has characteristics indicating success for RBCA implementation. Typically, those factors include the future use of the site as an industrial or commercial facility, the expense anticipated for remediation to background levels and the ability to control exposures to contamination based on natural and engineered barriers.

Assuming the team agrees that the RBCA approach makes sense, the responsible person should then set up a meeting between the representatives of the team and the applicable environmental regulators. During this discussion, a very basic site conceptual model should be used in order to explain the site characteristics, potential sources of contamination and the fundamental basis for using the RBCA approach in setting target cleanup levels. Based on the results of these negotiations, it is typically appropriate to memorialize the adoption of the

RBCA approach in the settlement agreement or consent order. Often, the cleanup action is initiated by some action taken against the responsible party by the regulatory agency. In those situations, a consent order is typically suggested by the environmental agency. The proposed consent order can specifically adopt the RBCA approach as the means for determining the appropriate cleanup levels.

Following agreement with the regulatory agency that RBCA should be used to establish cleanup levels, it is often a good idea for the responsible party to have meetings with other stakeholders, including the members of the community that may be impacted by the facility's contamination and other potential responsible parties at the site. Meetings with the stakeholders are important for both community relations and to foster recovery of environmental remediation costs from responsible parties. Because RBCA is still a relatively new process, community relations can be a very important part of the overall success of the RBCA strategy. Education of the stakeholders can very often make or break the success of the RBCA process, particularly with respect to obtaining approval of alternative cleanup levels by the environmental regulators.

Following these meetings, a workplan is typically developed and should be approved by the regulatory agency following an opportunity for comment by other stakeholders. Often it is appropriate to have your workplan as an attachment to any consent order or settlement agreement entered into between the regulatory agency and the responsible party.

V. Practical Problems and Possible Solutions to Key Issues in a RBCA Cleanup

Our experience has led us to conclude that there are certain issues that typically engender a substantial amount of discussion and/or negotiation during the RBCA process. It is important to realize that a successful implementation of a RBCA process requires a staged implementation. Not only are the cleanup decisions based on a tiered approach, but each step of the process upon which the cleanup decisions are based should be separately reviewed and consensus established with the stakeholders and the regulatory agency overseeing the cleanup. For example, the regulatory agency should approve the chemicals of concern identified for the site. Also, the appropriateness of the scope of site assessment, the selection of the receptors, identification of exposure pathways and exposure assumptions are all issues that should be fully discussed through separate deliverables in your workplan. Each of these important decision steps should be discussed and approved in step-wise fashion during the RBCA process. The following are a list of areas that typically engender negotiation and often have a substantial influence on the alternative cleanup levels.

Identification of Receptors - Identifying the human and ecological receptors is a critical step in the RBCA process. These receptors dictate the exposures to the contaminants and the hazard or toxicological criteria to be used to set RBSCs for the contaminants at the site. Typical receptors involve both on and off site workers, residents on or surrounding the site, casual visitors such as trespassers or invitees and other users or potential uses of the contaminated media including drinking water, recreational uses and aquatic life.

Exposure Assumptions - The assumptions used to determine the appropriate exposure levels in setting RBSLs are often highly debated among risk assessors. Many of these assumptions are based on standardized information. However, most standardized information is very conservative. Consequently, since the exposure assumptions can have a significant impact on the RBSCs, it may be appropriate to take specific measurements at the site to determine site specific exposure levels. For example, rather that assuming a 25 year employment record for a worker at a site, company records can be reviewed and analyzed to determine the average length of employment for an employee in the occupation that is identified as a receptor at the facility. Another example is exposures to vapors emanating from soil and groundwater contamination in buildings. Measurements of soil vapors in buildings may provide an important limitation on typical exposure assumptions that are found in most models modeling volatilization and exposure in indoor areas.

Point of Compliance - The point of compliance can have a substantial impact on meeting Tier 2 and Tier 3 standards. The "default" point of compliance is typically at the source. However, the point of compliance may very well be at the boundary of the site or at the particular receptor, provided that the exposure pathways identified at the site show that no exposure for the particular receptor occurs at the source of the contamination. Often the point of compliance with regard to groundwater contamination is a public policy decision determined by the state or local regulatory agency. However, even when the state has a rigid policy of on site (boundary line) containment of contaminants, temporary points of compliance (which can be off site for short periods of time) may be negotiated provided that the responsible person can establish that natural attenuation will eventually bring the point of compliance to within the boundary of the site or to the source.

Fate and Transport Models - Different models often dictate different results in your DAFs because of the sensitivities and assumptions built in to the models. Careful selection of the appropriate model can have a substantial impact on your Tier 2 and Tier 3 cleanup levels.

Concentration of site contamination - Determining the "real" concentration level of contaminants at the site can be based on one of two methods. Traditionally a deterministic analysis is used which assumes the highest concentration detected for a contaminant at a site that is representative of the contamination throughout the whole site. A probabilistic analysis, on the other hand, allows the use of models such as Monte Carlo, which evaluate more than just one sample concentration to determine the overall probable concentration for the contamination at the site. Often a probabilistic analysis will provide more flexibility in evaluating your cleanup concentration levels.

Time Dependant Variables - One important aspect of RBCA often involves natural attenuation of contaminants. Consequently, time to allow the attenuation or biodegradation process to complete it's beneficial result is often an important variable in obtaining a flexible, site specific, treatment level.

VI. Conclusion

The RBCA process is gaining acceptance in most circumstances. It is a valuable tool in managing all types of site contamination. It's application has gone beyond petroleum based contamination because the risk assessment principles apply to all of the traditional industrial site contaminants. RBCA should be advocated in any cleanup that involves more than a limited response.

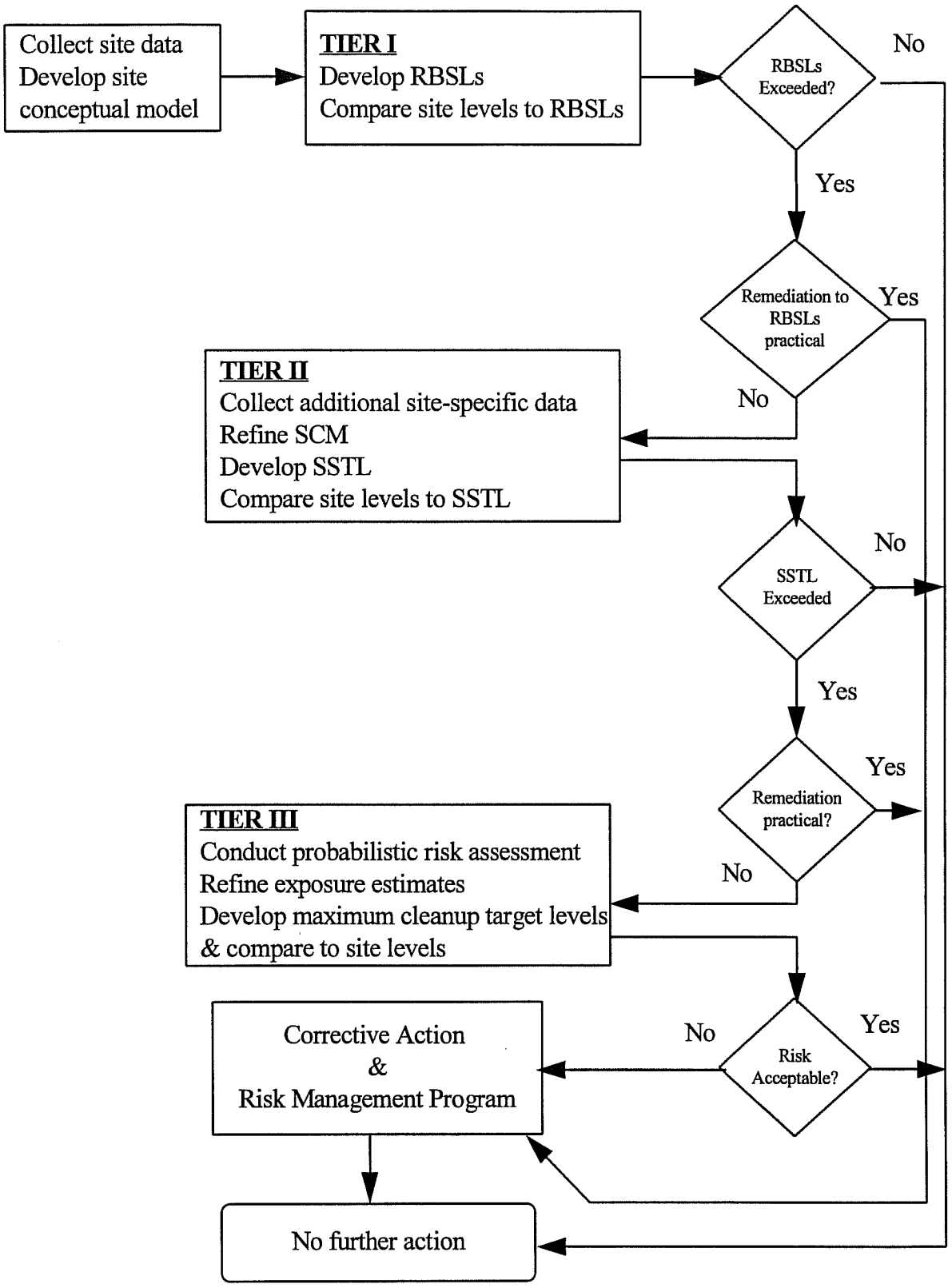

Figure 1. Risk assessment process flow chart; SCM = Site, conceptual model, RBSL = Risk based screening level, SSTL = Site specific treatment level.

Increased Emphasis on Toxics Control in Oil and Gas Industry NPDES Permits[1]

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ABSTRACT

The 1987 amendments to the Clean Water Act emphasized stricter control of toxics in wastewater discharges. Although state and U.S. Environmental Protection Agency permit writers have had the authority to incorporate strict water quality-based controls in permits, they did not widely use this authority in the past. However, general permits proposed in the past year by Region VI for discharges into the territorial seas of Louisiana and by Region X for coastal and offshore discharges in Alaska are much stricter than their predecessors. The Region VI permit requires numerical produced water limits on arsenic, lead, benzene, total phenols, radium, and whole effluent toxicity. The Region X permit requires numerical produced water limits on copper, arsenic, zinc, total aromatic hydrocarbons, total aqueous hydrocarbons, and whole effluent toxicity. The additional requirements increase the cost of complying with the permit, present more opportunities for exceeding one of the permit limits, and serve as a precedent for future permits. The industry should be prepared to accept the additional costs of these requirements or develop data to convince the regulatory agencies that the increased level of monitoring and permit limits is not necessary to protect water quality. Regulatory agencies should be receptive to new data provided by the industry and flexible in setting additional toxics controls.

THE CLEAN WATER ACT

In 1972, Congress passed amendments to the Federal Water Pollution Control Act that established a comprehensive program for water quality protection and water pollution control. This statute was later called the Clean Water Act (CWA). Two key goals of the CWA that are relevant to this paper are found in §101(a):

[1] Work sponsored by the U.S. Department of Energy, Office of Fossil Energy and Office of Policy, under Contract W-31-109-Eng-38.

"(1) it is the national goal that the discharge of pollutants into navigable waters be eliminated by 1985;" and

"(3) it is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited."

The first of these goals is not practical but is often cited as the basis for "ratcheting down" permit limits. The second goal is important and is the basis for much of the discussion in this paper.

The most important regulatory program established under the CWA is the National Pollutant Discharge Elimination System (NPDES). All point source discharges of pollutants to navigable waters (which include ditches and drainage pipes) must be authorized by an NPDES permit. More details on NPDES permits are provided in the next section.

In 1987, Congress amended the CWA to place a much greater emphasis on toxics. In particular, states were required to adopt specific numeric water quality standards for all toxic pollutants for which the U.S. Environmental Protection Agency (EPA) has published criteria and which could interfere with the designated uses of streams in that state. Most states have now adopted new toxics standards. As new NPDES permits are issued, they must include limits to ensure that discharges will not violate water quality standards.

NPDES PERMITS

Background

Although the NPDES program is a federal program, the EPA has delegated NPDES authority to 40 states. For those states that do not have NPDES authority, the local EPA region issues and enforces NPDES permits. This paper focuses on oil and gas industry permits issued by Region VI for Gulf of Mexico discharges and by Region X for Alaskan discharges.

NPDES permits may be issued for periods up to five years. In practice, a particular permit often remains in effect well beyond five years; if the permitting agency does not reissue the permit, the existing permit normally remains in effect indefinitely.

Most dischargers are covered under individual NPDES permits, but for the oil and gas industry, which has large numbers of facilities in the same geographic area with similar discharges, the EPA has issued general permits. General permits provide a set of operating and monitoring requirements; any facility that meets the eligibility criteria of a general permit can be covered by the general permit. Dischargers are not forced to seek coverage under a general permit, but most eligible dischargers choose to do so.

Calculation of Permit Limits

The most important part of most NPDES permits is the numerical limits for selected pollutants. Permits specify enforceable limits for metals, organics, and other more conventional pollutants, along with a monitoring schedule. The permit writer calculates permit limits by using two separate approaches and then chooses the more stringent of the two for each pollutant.

The first approach calculates technology-based limits. The limit is determined by the availability of cost-effective and dependable treatment technology and is set at a level that can be achieved by proper operation of such technology. For most major industrial categories, including the oil and gas industry, the EPA has published effluent limitations guidelines (ELGs) that establish national minimum technology-based standards.

The EPA's ELGs divide the oil and gas extraction industry into five subcategories: offshore, onshore, coastal, agricultural and wildlife water use, and stripper (40 CFR 435). This paper focuses on just the offshore and coastal ELGs.

Best practicable technology (BPT) limits, a first-tier level of treatment under the CWA, were adopted for each category on April 13, 1979 (44 FR 22075). More recently, the EPA updated the offshore and coastal ELGs. It promulgated final offshore ELGs on March 4, 1993 (58 FR 12454), and proposed coastal ELGs on February 17, 1995 (60 FR 9428). Final coastal ELGs are expected to be promulgated in November 1996. Both of these new ELGs contain best available technology (BAT) and new source performance standards (NSPS) limits. BAT and NSPS are an advanced level of performance applicable to existing and new source dischargers, respectively. During the many years prior to adoption of final BAT and NSPS for the offshore and coastal ELGs, permit writers had to rely on their best professional judgement of what would be appropriate technology-based limits.

The second approach for calculating permit limits is known as the water quality-based approach. Permit writers determine the allowable dilution and calculate the concentration of each pollutant that can be discharged and still meet water quality standards at the edge of a mixing zone. Each state has different water quality standards and mixing zone policies, so a wide range of possible water quality-based limits can be derived.

In several recent EPA general permits, limits for produced water were based on a combination of the technology-based and water quality-based approaches. Oil and grease limits were based on the ELGs, and limits on toxics and whole effluent toxicity were based on state water quality standards and water quality modeling.

INCREASED EMPHASIS ON TOXICS

Given the CWA goals of zero discharge of pollutants and no discharge of toxics in toxic amounts, it is not surprising that NPDES permit limits have become more stringent over the years. The general permits that have been proposed and issued in the past several years have required major changes in oil and gas industry operations. In some cases, reissued permits have required zero discharge of wastewater streams that had previously been discharged. In other cases, proposed new permits would require vastly more monitoring and more stringent limits on toxics. The following sections of this paper discuss several examples of the extent of the changes that have been made to discharge requirements as general permits have been reissued or proposed for reissuance.

Produced Water Discharges to Coastal Waters of Louisiana and Texas

In coastal waters of Louisiana and Texas, operators had discharged produced water for many years. A combination of state and EPA measures are leading toward zero discharge of produced water in coastal waters. The Louisiana Department of Environmental Quality (LADEQ) promulgated regulations in 1991 that required a phase out of coastal produced water discharges by January 1, 1995 (LAC 33:IX, 7.708). Based on some preliminary U.S. Department of Energy (DOE) comments, on December 16, 1994, LADEQ extended the deadline for discontinuing produced water discharges for certain open bay locations to January 1997. Texas regulations do not contain any specific prohibition for produced water discharges to coastal waters.

Region VI issued general permits LAG290000 and TXG290000 for produced water and produced sand discharges to coastal waters of Louisiana and Texas on January 9, 1995 (60 FR 2387). The permits required zero discharge for both produced water and produced sand. They were accompanied by a general administrative compliance order that provided a time extension until January 1, 1997, to meet the zero discharge requirement.

The EPA's proposed ELGs for coastal oil and gas operations also contain a zero discharge requirement for produced water and produced sand discharges to the Gulf of Mexico. Although discussions about extending the compliance date for the general permit and for meeting the new ELGs when they become effective are occurring during the summer of 1996 involving EPA Region VI, Texas, and Louisiana, it appears inevitable that sooner or later, Texas and Louisiana coastal operators will be required to meet zero discharge for produced water. The rationale for zero discharge is a combination of a cost-effective technology being available and in common use (underground injection) and the concern that produced water discharges may cause violations of state water quality standards.

Discharges to Louisiana Territorial Seas

On April 3, 1981, EPA Region VI issued general permit LA0060224 for discharges from oil and gas operations to the territorial seas of Louisiana (46 FR

20284). The territorial seas are the band of waters stretching three miles seaward from the coastline. Discharges to the territorial seas are covered under the offshore ELGs. The permit set limits based on BPT for the offshore subcategory of the ELGs. The permit contained oil and grease limits for produced water and specified no discharge of free oil for drilling fluids, drill cuttings, deck drainage, and well treatment fluids. The permit expired April 3, 1983, and was reissued on September 15, 1983 (48 FR 41494). Although that permit expired June 30, 1984, it was extended administratively to the present.

On July 19, 1996, Region VI proposed a new general permit LAG260000, which will replace LA0060224 when it is issued (61 FR 37746). The proposed new permit is much more stringent, incorporating BAT- and NSPS-level limits along with water quality-based limits on toxics. Table 1 summarizes the existing and proposed effluent limits for the major wastewater streams. Although the limits in the new permit are very restrictive when compared with those of the existing permit, one must remember that the existing limits have remained unchanged for more than 15 years.

Discharges to Outer Continental Shelf in Western Gulf of Mexico

On July 9, 1986, EPA Region VI issued general permit GMG280000 for discharges to the Outer Continental Shelf of the Gulf of Mexico (51 FR 24897). The permit conditions reflected BPT-level performance with some best professional judgement used.

On November 19, 1992, Region VI issued final general permit GMG290000 for discharges to the outer continental shelf in the western Gulf of Mexico (57 FR 54642). This permit, which replaced GMG280000, was subsequently modified on December 3, 1993, to incorporate provisions from the final offshore ELGs (58 FR 63964). The new permit is much more stringent, incorporating BAT- and NSPS-level limits along with water quality-based limits on toxics. Table 2 summarizes the previous and new effluent limits for the major wastewater streams.

Discharges to Cook Inlet, Alaska

On October 3, 1986, EPA Region X issued general permit AKG285000 for discharges to Cook Inlet (51 FR 35460). This permit was far more comprehensive than the comparable permit then in effect in Region VI, particularly for drilling fluids and drill cuttings. The permit contained limits on cadmium and mercury in the barite used to make up drilling fluids and required toxicity testing for drilling fluids.

Region X proposed a new general permit AKG285100 on September 20, 1995, to cover discharges to Cook Inlet (60 FR 48796). Cook Inlet is considered part of the coastal subcategory, and the coastal ELGs have not yet been finalized; some of the limits from the offshore ELGs were incorporated through best professional judgement. Other limits were chosen to meet Alaskan water quality

standards. Table 3 summarizes the existing and proposed effluent limits for the major wastewater streams.

DISCUSSION

The main conclusion that can be drawn from this evidence is that the latest round of permits issued to the oil and gas industry is significantly more stringent than previous permits. In some cases, this strictness is attributable to promulgation of final ELGs for the offshore subcategory. In other cases, it is attributable to an increased emphasis on toxics that was underscored by the 1987 amendments to the CWA. The latest permits include water quality-based limits on individual metals and organics as well as on whole effluent toxicity.

The increased complexity of the newer permits and the extra parameters that need monitoring create more opportunities for noncompliance with permit limits. Thus, dischargers must be increasingly diligent, not only about operating treatment facilities sufficiently to meet permit limits but also about coordinating the logistics of the expanded level of monitoring. The expense of the additional monitoring represents another complicating factor for offshore and coastal operators. Operators in these areas have been able to discharge for many years under relatively limited effluent requirements. Those days are past, and operators must be prepared to accept the additional costs of these requirements or develop data to convince the regulatory agencies that the increased level of monitoring and permit limits is not necessary to protect water quality.

The proposed Gulf of Mexico territorial seas permit offers the potential for reduced monitoring frequency when repeated samples show compliance with the permit limits. This type of flexibility helps to ease the monitoring burden somewhat. When permits are renewed, operators should seek this and other mechanisms for reducing the monitoring burden to a level that offers assurance to regulatory agencies without being unnecessarily costly.

As part of the shift toward greater stakeholder involvement, which should include the industry's concerns, regulatory agencies should be receptive to new data provided by the industry and flexible in setting additional toxics controls. Establishing provisions like the reduced monitoring frequency from the proposed Gulf of Mexico territorial seas permit mentioned above and allowing analytical results that are below a minimum quantification level to be reported as zero are good steps in that direction.

It is tempting to compare the stringency of Region VI and Region X general permits. In terms of limits and conditions, the Region X permits appear to be more stringent. On the other hand, drilling fluids, drill cuttings, and produced water discharges into coastal Gulf of Mexico waters are currently prohibited or will soon be prohibited yet discharges into Cook Inlet, also considered to be coastal waters, are permitted. When developing its general permits, each region needs to consider the location of the permitted facilities, the

nature of the water environment around those facilities, and the relevant state water quality standards and mixing zone policies, as well as the political climate within that region.

The U.S General Accounting Office recently reported on the differences among states in issuing NPDES permits (1). Its report found that in regulating toxic pollutants from municipal wastewater treatment facilities, some states consistently established numerical limits for toxics, while other states consistently imposed monitoring requirements. A few states placed neither permit limits nor monitoring requirements into their permits. Given the evidence from reference (1), it is not surprising that the Region VI and Region X general permits do not look the same.

REFERENCES

1. U.S. General Accounting Office, "Water Pollution, Differences among the States in Issuing Permits Limiting the Discharge of Pollutants," report GAO/RCED-96-42, January 1996.

Table 1

Summary of Limits from Existing General Permit LA0060224 and Proposed General Permit LAG260000 for Discharges to Territorial Seas

Discharge	Parameter	Limitations - LA0060224	Limitations - LAG260000
Drilling Fluids & Drill Cuttings		no discharge of free oil	zero discharge of fluids or cuttings
Produced Water	oil & grease	72 mg/l max.	29 mg/l avg. 42 mg/l max.
	chronic toxicity		depends on dilution
	arsenic, benzene, lead, total phenols		depends on dilution
Produced Sands			zero discharge
Deck Drainage	free oil	no discharge	no discharge
Well Treatment Fluids, Completion Fluids, & Workover Fluids	oil & grease	no discharge of free oil	29 mg/l avg. 42 mg/l max.
Misc. Discharges of Seawater and Freshwater to Which Chemicals Have Been Added	treatment chemicals		most stringent of: EPA label registration, manufacturer's recommended dose, or 500 mg/l
	free oil		no discharge
	acute toxicity		depends on dilution

Table 2

Summary of Limits from Previous General Permit GMG280000 and New General Permit GMG290000 for Discharges to the Outer Continental Shelf

Discharge	Parameter	Limitations - GMG280000	Limitations - GMG290000
Drilling Fluids & Drill Cuttings	free oil	no discharge	no discharge
	acute toxicity		30,000 ppm min.
	mercury & cadmium		limits placed on concentration in barite
Produced Water	oil & grease	48 mg/l avg. 72 mg/l max.	29 mg/l avg. 42 mg/l max.
	chronic toxicity		depends on dilution
	radium 226 & 228		monitor
Produced Sands		no discharge of free oil	zero discharge of produced sands
Deck Drainage	free oil	no discharge	no discharge
Well Treatment Fluids, Completion Fluids, & Workover Fluids	oil & grease	no discharge of free oil	29 mg/l avg. 42 mg/l max.

Table 3

Summary of Limits from Existing General Permit AKG285000 and Proposed General Permit AKG285100 for Discharges to Cook Inlet

Discharge	Parameter	Limitations - AKG285000	Limitations - AKG285100
Drilling Fluids & Drill Cuttings	acute toxicity	preapproval of additives based on toxicity	30,000 ppm min.
	mercury & cadmium	limits placed on concentration in barite	limits placed on concentration in barite
	chemical additives	provide list of additives	provide list of additives
	barium, cadmium, chromium, copper, mercury, zinc, and lead	monitor only	monitor only
Produced Water	oil & grease	48 mg/l avg. 72 mg/l max. (except for one platform with 15 mg/l avg. & 20 mg/l max.)	29 mg/l avg. 42 mg/l max. (except for one platform with 15 mg/l avg. & 20 mg/l max.)
	chronic toxicity		depends on dilution
	copper, arsenic, zinc, total aromatic hydrocarbons, & total aqueous hydrocarbons		depends on dilution
	cadmium, lead, nickel, & silver		monitor only
Produced Sands	free oil	no discharge	not listed in permit
Deck Drainage	free oil	no discharge	no discharge
	chronic toxicity (for production operations)		monitor only
Well Treatment Fluids, Completion Fluids, & Workover Fluids	oil & grease	no discharge of free oil	29 mg/l avg. 42 mg/l max.
	cadmium, copper, lead, nickel, silver, & zinc		monitor only

Effects of Title III of the Clean Air Act Amendments and MACT on Oil and Gas Production Facilities

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ABSTRACT

The oil and gas industry is faced with many important air quality issues today. One issue of primary concern is the emission of aromatic compounds, primarily benzene, toluene, ethyl benzene, and xylene (collectively known as BTEX), and other volatile organic compounds (VOC) from production operations. Regulatory agencies have identified the emission of BTEX and other VOC from oil and gas production operations as a significant contributor to air pollution. Sampling studies indicate that many previously unregulated production facilities could be considered major sources under Title III of the Clean Air Act Amendments of 1990, which governs the emissions of 188 hazardous air pollutants (HAPs). In addition to possible federal permitting requirements, many states are now considering regulating emissions from these operations.

This paper will focus on Title III of the Clean Air Act Amendments of 1990 (Air Toxics) and the effects it will have on oil and gas production facilities. It will present a look at maximum achievable control technology (MACT) requirements, who they affect, what should be done to prepare for MACT, and what effects it may have on a company. The paper will also briefly discuss the development of an emission inventory and which sources are likely to be subject to MACT requirements.

WHAT IS MACT AND WHO DOES IT AFFECT?

Recent information indicates that many oil and gas production facilities may be major sources under Title III due to emissions of BTEX compounds. It is estimated that there are over 40,000 glycol dehydration units operating in the United States[1] and nearly 40 percent of the units sampled as part of a Louisiana study in late 1989 and early 1990 would be considered major sources under Title III[2]. Other emissions coming under increased scrutiny from the regulatory agencies are those emissions resulting from the flash losses as liquids enter an atmospheric tank downstream of a high pressure separator.

MACT is defined as the "...maximum degree of reduction in emissions of the hazardous air pollutants subject to this section [Section 112 of the Act] (including prohibition on such emissions, where achievable) that the Administrator, taking into consideration the cost of achieving such emission reductions, and any non-air quality health and environmental impacts and energy requirements, determines is achievable for new or existing sources in the category or subcategory to which such emission standard applies..." The categorical emission standards must be achieved by any stationary source or group of stationary sources within a contiguous area and under common control that emit, or have the potential to emit, in the aggregate 10 tons per year of more of any HAP or 25 tons per year or more of any combination of HAPs. These thresholds define a major source of air toxics.

The potential to emit is defined as "the maximum capacity of a stationary source to emit a pollutant under its physical and operational design." In addition, any physical or operational restriction that limits emissions from a source may be considered as part of its design if the limitation, or the effect it would have on emissions, is federally enforceable. Examples of federal enforceability could be the limitation on hours of operation appearing in an air quality operating permit or the requirement to operate a control device such as a condenser or flare.

MACT for new sources will not be less stringent than the best controlled similar source within the category, while MACT for existing sources will determined according to the number of sources in the category. For categories with more than 30 sources the "MACT Floor" will not be less stringent than the average level of control achieved by the best performing sources in the category.

Oil and gas facilities receive somewhat of a break in the definition of a major source due to the non-aggregation rule for HAPs. This states that "...emissions from any oil and gas production well (with its associated equipment) and emissions from any pipeline compressor or pump station shall not be aggregated with emissions from other similar units, whether or not such units are in a contiguous area or under common control, to determine whether such units or stations are major sources."

This allows separate wells and their associated equipment to be considered separately even when located in close proximity one another.

For each MACT standard there are at least two levels of control requirements: MACT for new sources and MACT for existing sources. Also, for each source category, there will be at least two rounds of MACT. The first will be the Presumptive MACT where MACT will be defined regardless of risk. The second will be the Residual Risk MACT. This second round will follow the Presumptive MACT by eight years and set new standards based on risk. A review will occur every eight years thereafter.

The MACT standard for oil and gas production is due to be promulgated by November 15, 1997. Currently, it is expected that the standards will be proposed in late 1996 or early 1997. The production sources that will be affected by the standard are likely to be glycol dehydrators and associated equipment, tanks where flash losses could occur (those at atmospheric pressure and immediately downstream of a separator), and storage tanks with the potential for large evaporative losses such as those storing a high gravity condensate. In addition, a monitoring and maintenance program may have to be established for fugitive equipment leaks at gas plants.

The control technology approaches allowed in order to comply with the standards include, but are not limited to:

- reduction in volume or elimination of emissions due to process changes or material substitution;
- enclosing of systems or processes to eliminate emissions;
- collection, capture and/or treating of emissions;
- development of design, equipment, work practice, or operational standards to reduce or eliminate emissions; and
- any combination of the above.

New and reconstructed sources will be required to be in compliance on the effective date of the standard, sources with initial start-up after the effective date of the standard will need to be in compliance on start-up, and there are special provisions for sources that begin construction between the proposal and promulgation dates. Existing sources will have to be in compliance by the compliance date in the standard or no later than three years after the effective date of the standard if no compliance date is specified. It should be noted that major sources under Title III require a Title V operating permit whether or not they are currently subject to a MACT standard and whether or not they are on the source category list.

PREPARING FOR MACT

There are a number of things companies can do to prepare for MACT. The first, and perhaps the most important, is to determine HAP emissions from the sites in question through preparation of an emission inventory. The purpose of the emission inventory is to gather, review, and verify all information related to each emission source at the site. The calculated emissions will then serve as the basis for determining applicability of MACT, as well as all permitting and compliance activities at the site. The emission inventory consists of the following five steps:

(1) Identify sources and define emission units;

(2) Identify maximum capacity for plant sources and all source parameters;

(3) Map sources and develop stack parameters;

(4) Calculate actual emissions and potential to emit (PTE);

(5) Identify regulatory requirements.

The primary objective of the emission inventory is to develop accurate emission estimates for each of the sources at the site. It should be kept in mind that the preferred hierarchy for emission calculations is measured emissions data, mass balance, emission factors, and then engineering calculations.

It is important to make sure that all sources of emissions are accounted for in the emission inventory. Sources that have recently been in the regulatory spotlight, and that have not traditionally been considered in emission inventories, include glycol dehydrator still vent emissions and flash losses in atmospheric tanks downstream of high pressure separators.

After completion of the emission inventory, if it is determined that MACT will likely be applicability to the facility, options that could allow the site to possibly avoid MACT should be investigated. These options include source sampling to obtain a more accurate estimate of emissions, making process modifications that will lead to a reduction in emissions, adding controls that will reduce emissions to levels below the MACT thresholds, and obtaining operating restrictions through a federally enforceable state operating permit (FESOP). In most cases, permitting an add-on control device through a federally enforceable program will be required in order to allow calculation of PTE after the control device. Any mechanism to limit emissions requires a state permit and must be in place before the first compliance date of the MACT standard, if MACT requirements are to be avoided.

Once it is determined that MACT will apply, the person or group responsible for compliance at the site should further prepare to meet the requirements of MACT by:

- developing a cost estimate for expected MACT at the site;
- participating in discussions with EPA;
- studying other proposed and promulgated MACT standards;
- learning the application of the rules, how the state interprets the rules, and how they fit with current state air toxics rules; and
- planning carefully for compliance (i.e., determining how to meet or exceed requirements with enough buffer to ensure continuous compliance).

IMPACTS ON THE COMPANY

For companies with facilities that are determined to be major sources under Title III and subject to MACT requirements, there could be significant costs associated with achieving and maintaining compliance. There will be direct costs (both capital and operating) for controls and/or process modifications, costs associated with record keeping and reporting requirements, and costs associated with a possible loss in operating flexibility. The company will need to devote resources to prepare for enforcement, train personnel in compliance and accident prevention, and be prepared to answer the question of risk, because it will be asked.

CONCLUSION

In summary, the requirements MACT will place on oil and gas sites that are considered "major" under Title III could be significant. Many sources which were previously unregulated could be forced to make process modifications, add controls, and develop and implement strict record keeping and reporting procedures. The entire process, from the first emission estimates to operating under the MACT standards could be both costly and time consuming. However, a thorough understanding of the subject facility, the MACT standards, and the application of the rules will make it much easier to make the transition from operating today to operating under MACT.

REFERENCES

1. Thompson, Patrick A., Espenschied, AndrewP., Myers, Duane B., and Berry, Craig A., 1994, "Technical Reference Manual for GRI-GLYCalc™: A Program for Estimating Emissions from Glycol Dehydration of Natural Gas," Gas Research Institute, GRI-94/0228, Chicago, IL, p. 2-1.

2. Texas Natural Resource Conservation Commission, Permits Division, Emission Factors for Glycol Dehydrators from Louisiana Department of Environmental Quality Study.

Update on Federal Air Quality Regulatory Developments Affecting the Petroleum Industry

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A lack of resources and the emphasis on regulatory reform has hindered EPA in its efforts to implement provisions of the 1990 amendments to the federal Clean Air Act. Nevertheless, EPA has taken some actions on several programs that affect the petroleum industry.

This paper will focus on developments in federal air quality regulations that impact the petroleum industry, including maximum achievable control technology for hazardous air pollutants, risk management plans, operating permits and reforms to new source review requirements. The paper will also address state implementation of the federal programs and provide suggestions for influencing the development and administration of these programs.

CLEAN AIR ACT INTRODUCTION

Few significant changes in the regulation of air pollution in this country occurred from 1977 until 1990. This was primarily the result of disputes between the legislative and executive branches of the federal government that precluded changes to the federal Clean Air Act[1] ("FCAA"). The absence of new federal legislation caused state regulation also to be primarily limited to administration of the programs that already existed. During this period, "old" problems such as urban smog and regulation of hazardous air pollutants, continued beyond the statutory deadlines established for their elimination. Additionally, concerns about "new" problems were advanced, including such items as acid rain, ozone depletion and global warming. Finally, in 1990, Congress adopted and the President signed into law a massive package of amendments to the FCAA.[2] The Environmental Protection Agency ("EPA") began the complex task of implementing the new statutory provisions while balancing the interests of state and local government, regulated entities, and the public. Early optimism for smooth implementation has faded as a result of missed deadlines and lawsuits. Significant developments are occurring, however, many of which directly affect the petroleum industry.

Historically, the oil and gas industry, particularly the exploration and production portion of the industry, has been the subject of special treatment in the area of air pollution control. The 1990 amendments to the FCAA continued that trend and EPA and many of the states are working with the regulated community in the development of regulations and programs implementing the 1990 amendments.

A. State and Federal Permitting Requirements

1. Permitting New or Modified Sources

a. Federal Requirements

The FCAA requirements for permitting new or modified sources ("NSR") are limited to stationary sources. The FCAA establishes two NSR permitting programs: one for nonattainment areas[3] and the other for the attainment areas.[4] The permitting program for the attainment areas is called Prevention of Significant Deterioration ("PSD"). In both programs, only new major sources and major modifications require a permit and the permit must be obtained before construction may commence. Both programs also use a plant-wide definition of the term "source" that includes all pollutant emitting activities from buildings, structures, facilities or installations that are on the same or contiguous properties and under common control, and have a Standard Industrial Classification ("SIC") code number with the same first two digits.[5] There is a complicated system for

evaluating changes to an existing facility to determine whether a major modification will occur[6]

There are certain differences between the PSD permitting program for attainment areas and the permitting program for nonattainment areas. One difference is in the criteria used to determine which sources are required to obtain a permit. There are more significant differences between these two programs in the demonstrations that must be made to actually obtain the permit.[7] The nonattainment permit requires a more stringent level of control technology known as the "lowest achievable emission rate" ("LAER") which is based on the most stringent level of control that is actually achieved or required in any state for that type of source. Nonattainment permits also require the increase in emissions of the nonattainment pollutant from the proposed source to be "offset" by an even greater reduction in emissions of the same air pollutant from a source in the same general area. Additionally, to obtain a nonattainment permit, an analysis of alternative sites must be made and the permit applicant must certify that all other major sources in the state controlled by the applicant or by those who control the applicant are either in compliance or on a schedule for compliance with all applicable air pollution requirements. Provisions that are unique to the attainment area "PSD permit" include the potential for significant preconstruction monitoring of existing air quality and a determination that increases in the ambient concentrations of the air pollutant which is the subject of PSD review from the proposed source and other sources occurring after a specified "baseline date"[8] do not exceed a level prescribed in the rules.[9]

EPA has proposed a number of significant reforms to its NSR program.[10] The reforms were developed in part upon the efforts of a work group representing both environmentalists and the regulated community that worked for over a year on NSR issues. The workgroup did not achieve consensus on a number of major issues, but the discussions helped form the framework for the EPA proposals. The proposed reforms include:

1. A "clean unit" exemption allowing many changes to occur at already well controlled units without the need for NSR;

2. New methodology for determination of a plant's existing baseline emissions which will enable the plant to use any 12 consecutive months in the past ten years;

3. Allow NSR to be determined by comparing existing actual emissions to future actual emissions;

4. Allow many pollution control projects to be excluded from NSR;

5. Allow establishment of a voluntary plant-wide emissions cap with exemption from NSR for most changes in a plant that do not exceed the cap;

6. Greater allowance of emission reductions from shutdowns to be used as credits.

While the federal permitting requirements can significantly impact petroleum refining and natural gas processing operations, most exploration and production activities have emissions that normally would not trigger the federal permitting requirements. This is fortunate because satisfying the federal requirements can significantly increase costs and cause significant delays in planned construction and development.

b. State Requirements

Most states operate new source review permitting programs. Some of these state programs do not add significantly to the federal new source review programs; others are substantially more comprehensive. Many states require permits for minor sources and modifications and require use of the best available control technology for all air pollutants emitted by the source, not just the pollutants for which NAAQS have been established. In determining whether a modification will take place, some states, unlike the federal practice, do not allow emission reductions that have occurred or will occur to be counted against emission increases. Thus, only the increases are considered to determine if there is a modification. In order to obtain the permit, the applicant may have to demonstrate that emission impacts will be acceptable. This may include consideration of the potential for odorous emissions to interfere with the normal use and enjoyment of property. Exemptions from the state permitting requirements may be established for certain categories of small sources. Additionally, there is a trend towards "licensing by rule" under which a category of sources meeting objective criteria established in the rule are considered to be permitted by the authority of the rule without the need for a detailed, site specific permit application. As an example, the State of Texas adopted a permit by rule (referred to as "Standard Permit") for oil and gas production facilities.[11]

2. Permitting of Existing Sources - Title V Operating Permits

Among the most significant changes made by the 1990 amendments to the FCAA was the establishment of an operating permit program applicable to existing as well as new sources.[12] Sources required to obtain an operating permit include major sources as defined in the attainment and nonattainment programs described above as well as "major" sources under the new hazardous air pollutants program and sources subject to NESHAPs and NSPS.[13] The purpose of the program is to include all of the SIP requirements as conditions of the permit, require enhanced monitoring of emissions, and emphasize compliance by requiring owners of the sources to periodically certify the source's compliance status.

The FCAA directs that the states should implement the program and imposes sanctions for those states that fail to meet those requirements. The EPA rules establishing the minimum requirements for an approvable state program[14] prompted lawsuits and attempts at reproposal. Currently, EPA has adopted policy changes and proposed amended rules to address a laundry list of controversial issues. Many of the states have commenced approved operating permit programs and other states are close to receiving approval.

Most larger oil and gas operations, such as refineries and gas processing plants, will be required to obtain the new operating permit. Smaller sources such as those in the exploration and production sector (other than gas processing plants) may not trigger the operating permit requirements. The federal rules[15] provide a benefit to the industry because they provide that emissions from any oil or gas exploration or production well (and associated equipment) and from pipeline compressors or pump stations will not be aggregated with emissions from similar units located on contiguous or adjacent properties under common control to determine whether the source triggers the federal operating permit requirement as a major source for hazardous air pollutants. This will substantially reduce the potential for such sources to be required to obtain an operating permit.

The states may adopt "general permits," which are permits by rule that would eliminate the necessity of a detailed, site-specific application. Although it is unlikely that general permits would be established for larger sources such as refineries, owners of oil and gas exploration/production facilities may well wish to urge their states to adopt standard permits that would cover their operations.

B. Specific Rules with Significant Impact on the Petroleum Industry Operations

In addition to the permitting requirements, environmental agencies have adopted a large number of rules regulating specific sources and air pollutants. These rules often apply to both existing and new sources and frequently are adopted to address specific concerns. The following discussion will identify specific rules that significantly impact oil and gas operations.

1. Hazardous Air Pollutants Program

The original NESHAP program as established in the 1970 Act proved difficult for EPA to implement. Judicial construction of the statutory provisions effectively paralyzed the program resulting in EPA regulating only eight hazardous air pollutants.

The paralysis that afflicted the NESHAP program led Congress in the 1990 amendments to the FCAA to make sweeping changes to the hazardous air

pollutants program including a switch in the philosophy of how to regulate those pollutants. Instead of studying the toxicity of chemicals before regulation, Congress listed 189 chemicals as hazardous and directed that emissions of those chemicals be reduced.[16] EPA may revise the list to add or delete chemicals and persons may petition EPA to make such revisions.[17] The mechanism for reduction is the installation of maximum achievable control technology (MACT) on major sources and MACT or generally available control technology (GAT) on area sources. A major source is any stationary source that has the potential to emit either 10 tons per year ("tpy") or more of any of the 189 hazardous air pollutants (HAP) or 25 tpy or more of the 189 HAP combined; an area source is any stationary source of HAP that is not major.

Pursuant to an FCAA provision, EPA has promulgated a list of major and area source categories that will be regulated, along with the dates by which the regulations establishing MACT or GAT will be promulgated for those source categories.[18] Three different dates have been established for all categories: November 15, 1994, 1997, or 2000. If EPA fails to promulgate the regulation establishing MACT for a category or subcategory of major sources by the deadline, the owner or operator of a major source in that category or subcategory must submit a permit application to the EPA (or delegated state) within 18 months of the missed deadline.[19] Issuance of the permit will be conditioned on the source using MACT as established on an *ad hoc* basis in the permit review.

2. Petroleum Refinery MACT

On August 18, 1995, EPA published its final rules under NESHAPS establishing MACT for petroleum refineries.[20] The rules apply to petroleum process refining units and associated miscellaneous process vents, storage vessels, wastewater streams, equipment leaks, marine tank vessel loading operations and those gasoline loading racks classified under SIC Code 2911. The last two categories were included in the final rule to facilitate averaging of emissions among emission points to achieve compliance. Catalyst regeneration vents on catalytic cracking units and catalytic reforming units and vents from sulfur recovery units were not included but will be addressed in future NESHAPS promulgations. The standards are applicable to affected sources that emit or have equipment containing or contacting any of the hazardous air pollutants listed in the rule. The following control requirements are contained in the rules:

Miscellaneous Process Vents

Those vents that cannot reduce volatile organic compound emissions to less than or equal to 72 pounds per day (lbs/day) for existing sources and 15 lbs/day for new sources must be controlled by flaring, or by use of controls that reduce organic hazardous air pollutants by 98% or to 20 or less parts per million by volume.

Storage Vessels

The storage vessels requirements vary between new and existing sources, vessel capacity, and the vapor pressure and concentration of hazardous air pollutants in the stored liquid. The required controls include internal or external floating roofs with proper seals or a closed vent system with a control device that reduces hazardous air pollutant emissions by 95% or to 20 or less parts per million by volume.

Wastewater

Wastewater streams at a refinery with a total annual benzene loading of at least 10 megagrams of benzene per year which are not exempt from the control requirements of the existing benzene waste regulations of NESHAP must comply with the provisions of that benzene NESHAP. (40 C.F.R. Part 61 Subpart FF).

Equipment Leaks

Existing sources may either meet the standards in 40 C.F.R. Part 60 Subpart VV (NSPS for equipment leaks) or 40 C.F.R. Part 63 Subpart H (Hazardous Organic NESHAP). New sources must meet the provisions of the Hazardous Organic NESHAP.

Marine Tank Vessel Loading and Gasoline Loading Racks

Marine tank vessel loading and gasoline loading racks must comply with the provisions of 40 C.F.R. Part 63 Subparts Y and R, respectively.

As is typical with NESHAP promulgations, the petroleum refinery MACT contains significant monitoring and record keeping requirements. Compliance with the petroleum refinery MACT standards at an existing source may be accomplished by emissions averaging; that is, overcontrolling certain emission points and undercontrolling others such that the total amount of emissions from all points does not exceed the sum of the allowables for each point. The standards for equipment leaks, however, may not be included in emissions averaging. New sources are not allowed to use emissions averaging.

The final rules were criticized by industry as based upon outdated information and overly burdensome. Unsuccessful attempts were made in Congress to severely limit funding for enforcement of the final rules. EPA has continued to meet with industry representatives to develop mechanisms to minimize the paperwork burden and also intends to publish by the end of the year minor proposed changes to the storage tank applicability provisions.

3. Oil and Gas MACT

EPA has encountered substantial difficulties in developing proposed MACT for oil and natural gas production facilities. EPA expected to publish proposed rules in early 1995; currently, publication is scheduled for February 1997. The draft under consideration would establish control standards for glycol dehydrator unit process vents, containers, surface impoundments and equipment leaks. Glycol dehydrators would be listed as an area source and certain glycol dehydrators would be required to implement controls. Early draft versions suggested that up to 40% of glycol dehydrators would be required to add controls, but later versions appear to have reduced that number. EPA was contemplating not requiring controls unless the processing rate equals or exceeds three million standard cubic feet per day and benzene emissions are greater than one ton per year. EPA plans to establish an additional provision that would further minimize the number of dehydrators subject to controls based on proximity of the units to inhabited areas.

Another problem that has delayed the proposal is the definitions associated with the determination of what constitutes an oil and gas "source." The FCAA provides that emissions from an oil or gas well and associated equipment will not be aggregated with emissions from other similar units to determine whether such units are a major source of HAP. EPA originally contemplated a narrow definition of what constitutes a well and associated equipment limiting it to the well and pressure maintenance or flow control devices also known as the "Christmas Tree." This narrow definition had the potential to subject more oil and gas operations to MACT and operating permit requirements. EPA, however, also considered limiting the size of a "facility" by defining it to be only the aggregate of all equipment within 1 kilometer (0.6 mile) of each other and include no more than one well and no more than one pipeline compressor or pump station.

EPA currently believes that the definition of associated equipment should be expanded to include equipment up to the point of custody transfer for an oil well and up to the entrance of a gas plant. There would be two exceptions however: glycol dehydrators and tanks with flashing potential would not be considered associated equipment. The concept of a distance limitation on the size of a facility is being discarded because of concerns over legal authority.

4. Accidental Release Prevention and Risk Management Plans

EPA is moving forward on the program required by the FCAA to address accidental releases of certain air pollutants.[21] On January 31, 1994, EPA published final rules that list the substances that pose a significant hazard if accidentally released and established threshold quantities that, if exceeded, would require preparation of a substantive risk management plan.[22] Hydrogen sulfide and methane were listed with threshold quantities of 10,000 pounds.[23] The

threshold quantity at a plant is determined by the amount of the chemical contained in a process, which includes all activities that use, store, manufacture, handle or move the chemical. Vessels involved in such activities that are interconnected or located such that all could be involved in a single accidental release situation are considered to be part of a single process.[24]

On April 15, 1996,[25] EPA proposed to amend these rules to provide that prior to entry into a natural gas processing plant or a petroleum refining process unit, regulated substances in naturally occurring hydrocarbon mixtures would not be considered in the calculation of the threshold quantity of those substances. Naturally occurring hydrocarbon mixtures would include any combination of condensate, crude oil, field gas, and produced water. Additionally, EPA proposed that a naturally occurring hydrocarbon reservoir is not a stationary source for the purposes of the accidental release program. Final action on these proposed changes is expected within nine months; on June 20, 1996, EPA stayed the effectiveness of those existing provisions affected by the proposed amendments until final action.[26]

The substantive risk management plan rules, proposed in October 1993, were not promulgated until May 1996 due to numerous controversial issues.[27] The final rules classify sources subject to the program into three tiers labeled Programs 1, 2, and 3; the programs are based upon process information so that a source with multiple processes could be subject to more than one program. Program 1 is available to any process that has not had an accidental release with off-site consequences in the five year period prior to submission of the risk management plan and has no public receptors within a specified distance associated with a worst case release scenario. All other processes are under Program 2 except for processes in specified Standard Industrial Classification codes, including 2911, petroleum refineries, which are under Program 3. Sources subject to the rules must submit a risk management plan, conduct a worst case release scenario analysis, and perform a five year accident history. There are additional requirements with sources in Programs 2 an 3 subject to more comprehensive provisions including analysis of alternative release scenarios. The worst case scenario is defined as the release of the largest possible quantity of a regulated substance from a vessel or process line and does take into consideration administrative controls and passive mitigation measures such as drains and dikes. Alternative release scenarios are more realistic excursions with less serious consequences.

5. Global Warming

Concerns over emissions of methane have been raised because methane is believed to be a "greenhouse effect gas" that contributes to global warming. In response, Congress, in the 1990 amendments, directed EPA to study and report to Congress on ways to reduce methane emissions that "are economically and technically justified with and without consideration of environmental benefit."[28]

One of the areas specifically directed for study was methane emissions associated with natural gas extraction, transportation, distribution, storage and use.[29] The report was to provide an inventory of methane emissions from accidental and intentional releases from natural gas and oil wells, pipelines, processing facilities and gas burners.[30] EPA completed the report and determined that oil and natural gas activities are responsible for ten percent of all methane emissions in the United States. The report identified the primary points of emissions as being fugitives from the well, releases from high bleed devices and dehydrators. The report identified what are believed to be cost-effective controls such as directed inspection and maintenance programs and replacing high-bleed pneumatic devices. In response to the report, EPA has established the Natural Gas STAR program, a voluntary EPA/Industry partnership. The program encourages natural gas companies to voluntarily institute "best management practices" to reduce methane emissions. Concerns regarding additional regulation have recently increased in response to reports that the Clinton administration now favors mandatory emission reductions to reach the goals of the 1992 Rio de Janeiro treaty.

6. Volatile Organic Compounds

In its regulation of volatile organic compounds in ozone nonattainment areas, Congress again made an effort to provide relief to some aspects of oil and natural gas production. Section 819 of the 1990 FCAA amendments (not codified into the FCAA) provides that the additional nonattainment requirements established in the 1990 amendments would not apply to the production of and equipment used in "the exploration, production, development, storage or processing of" oil or natural gas stripper wells located in marginal and moderate nonattainment areas and serious nonattainment areas having a population below 350,000.

C. Participation in Regulatory Developments

The combination of existing and anticipated budget cuts and the perceived backlash against governmental regulation has resulted in significant opportunities for the regulated community to influence regulation development.

Accordingly, opportunities exist to attempt to minimize the costs of regulation. Trade associations are usually the most effective in influencing regulatory development. Participation as early as possible in the process is a key to effectiveness. It is much easier to influence regulatory programs in the early stages of development rather than later, when the natural tendency of an agency is to defend the work it has done.

1. 42 U.S.C.A. §§ 7401 *et seq.* (1983 & West Supp. 1994).

2. Clean Air Act Amendments of 1990, Pub. L. No. 101-549, §§ 101-1101, 104 Stat. 2399, 2399-2712 (1990).

3. 42 U.S.C.A. § 7502(c)(5) (1983 & West Supp. 1994).

4. 42 U.S.C.A. §§ 7470-7479 (1983 & West Supp. 1994).

5. 40 C.F.R. §§ 52.21(b)(4)-(6), 51.165(a)(1)(i)-(iii) (1993).

6. 40 C.F.R. §§ 52.21(b)(1)(i)(C), 51.165(a)(1)(iv)(A)(2) (1993).

7. *Compare* 42 U.S.C.A. § 7503 (1983 & West Supp. 1994) *with* 42 U.S.C.A. § 7475 (1983).

8. 40 C.F.R. § 52.21(b)(14)(i) (1993).

9. 40 C.F.R. § 52.21(c) (1993).

10. 61 Fed. Reg. 38250 (July 23, 1996).

11. 30 Tex. Admin. Code § 116.610.

12. 42 U.S.C.A. §§ 7661-7661f (1983 & West Supp. 1994).

13. 42 U.S.C.A. § 7661a(a) (1983 & West Supp. 1994).

14. 40 C.F.R. Part 70.

15. 40 C.F.R. § 70.2("Major Source")(1)(i) (1993).

16. 42 U.S.C. § 7412(b)(1).

17. 42 U.S.C. § 7412 (b)(2)-(3).

18. 58 Fed. Reg. 63941 (December 3, 1993).

19. 42 U.S.C. § 7412(j).

20. 60 Fed. Reg. 43244 (August 18, 1995) (codified at 40 C.F.R. § 63.640).

21. 42 U.S.C.A. § 7412(r) (1983 & West Supp. 1994).

22. 59 Fed. Reg. 4478 (Jan. 31, 1994) (codified at 40 C.F.R. § 68).

23. 59 Fed. Reg. 4478 (Jan. 31, 1994) (codified at 40 C.F.R. § 68.130 (Table I)).

24. 59 Fed. Reg. 4478 (Jan. 31, 1994) (codified at 40 C.F.R. § 68.3).

25. 61 Fed. Reg. 16598 (April 15, 1996).

26. 61 Fed. Reg. 31731 (June 20, 1996).

27. 61 Fed. Reg. 31668 (June 20, 1996) (codified at 40 C.F.R. Part 68).

28. Clean Air Act Amendments of 1990, Pub. L. No. 101-549, § 603(a), 104 Stat. 2399, 2653 (1990).

29. Clean Air Act Amendments of 1990, Pub. L. No. 101-549, § 603(b)(1), 104 Stat. 2399, 2653-4 (1990).

30. Clean Air Act Amendments of 1990, Pub. L. No. 101-549, § 603(b)(1), 104 Stat. 2399, 2653-4 (1990).

Do Produced Water Toxicity Tests Accurately Measure the Produced Water Toxicity in Marine Environments?

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ABSTRACT

U.S. Environmental Protection Agency (EPA) Region VI has issued a general permit for offshore oil and gas discharges to the Gulf of Mexico that places numerical limits on whole effluent toxicity (WET) for produced water. Recently proposed EPA general permits for other produced water discharges in Regions VI and X also include enforceable numerical limits on WET. Clearly, the industry will be conducting extensive produced water WET testing. Unfortunately, the WET test may not accurately measure the toxicity of the chemical constituents of produced water. Rather the mortality of test organisms may be attributable to (1) the high salinity of produced water, which causes salinity shock to the organisms, or (2) an ionic imbalance caused by excesses or deficiencies of one or more of seawater's essential ions in the test chambers. Both of these effects are likely to be mitigated in actual offshore discharge settings, where the receiving water will be seawater and substantial dilution will be probable. Thus, the additional salinity of produced water will be rapidly assimilated, and the proper marine ionic balance will be quickly restored. Regulatory authorities should be aware of these factors when interpreting WET test results.

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INTRODUCTION

On November 19, 1992, the U.S. Environmental Protection Agency (EPA) Region VI issued final general permit GMG2900000 for discharges to the outer continental shelf in the western Gulf of Mexico (57 FR 54642). Among other monitoring requirements, the permit places numerical limits on whole effluent toxicity (WET) for produced water, the brine that comes to the surface along with oil and gas. Two other more recently proposed EPA general permits also include numerical limits on WET for produced water. Region X proposed general permit AKG285100 on September 20, 1995, to cover discharges to Cook Inlet (60 FR 48796). Region VI proposed general permit LAG260000 on July 19, 1996, for discharges to the territorial seas of Louisiana (61 FR 37746).

It is obvious that the EPA is interested in controlling toxicity in produced water discharges and that the oil and gas industry will be conducting many WET tests in upcoming years. Produced water can be toxic to marine indicator organisms in acute and chronic toxicity tests, creating the potential for noncompliance with permit limits. In most cases, dischargers that cannot meet their WET limits will dispose of produced water through costly injection wells. These three general permits cover hundreds of dischargers, primarily in the Gulf of Mexico (1). Although the potential economic impact to these dischargers of failing to meet WET limits cannot be accurately estimated at this time, it could be many million dollars.

Given the potential large costs of noncompliance with WET limits, it is appropriate to closely examine exactly what the WET test is measuring. This paper discusses the nature of produced water toxicity and the potential impacts of recent research on the requirements for marine organisms used in the regulatory interpretation of produced water toxicity test results.

HISTORICAL BACKGROUND

The 1972 amendments to the Federal Water Pollution Control Act formed the basis of what is now known as the Clean Water Act (CWA). The CWA included as a national policy that the discharge of toxic pollutants in toxic amounts would be prohibited. The CWA established the National Pollution Discharge Elimination System (NPDES) and required that NPDES permits set limits on the basis of available technology and, where needed, on water quality standards. In the early years of the NPDES program, the greatest emphasis was placed on controlling individual chemicals; little attention was given to the composite toxicity of effluents. Subsequent CWA amendments, particularly those passed in 1987, placed a much greater emphasis on toxics. Beginning in the late 1980s, EPA headquarters encouraged permit writers in states and EPA regions to incorporate WET

testing and WET limits in NPDES permits to protect against discharges of toxic pollutants in toxic amounts.

The EPA has developed and refined methodologies for evaluating toxicity of effluents to a variety of freshwater and marine organisms (2, 3). These tests were not designed to determine the actual effect on the receiving water community but rather to gauge the relative toxicity of various effluents to model or "indicator" organisms. Attention was given to organisms that were not only appropriately sensitive to potential toxicants, but also readily available and resistant to laboratory manipulation. The data from these tests were eventually used to develop permit requirements for WET. One important realization for the scientific community was that a number of effluents that were meeting water quality-based limits were toxic to indicator organisms. It was assumed that this toxicity resulted from the effects of multiple pollutants acting on the organism.

TOXICITY OF PRODUCED WATERS

Produced water is saline water brought to the surface along with oil and gas. The ratio of produced water to oil or gas increases as a well ages and can be as great as 98% of the total volume of extracted fluids (4). In offshore and many coastal areas, produced waters are typically discharged into the sea after receiving some treatment. The volume of discharged material can be enormous; nearly a billion barrels per year of produced water is discharged into the offshore Gulf of Mexico alone (1). Toxicity in produced waters has been observed by using various toxicity indicator organisms, and LC50s as low as 0.05% have been reported, although the average is typically greater than 10% (5). These data indicate that solutions containing these percentages of effluent killed half of the test organisms during the test.

The potential effects of produced waters on marine ecosystems have been debated in the literature, with much emphasis being placed on the potential impacts of hypersalinity, temperature, ammonia, hydrocarbons, and trace elements in large-volume discharges. Offshore platforms have been observed to attract high numbers of various marine species. The presence of large, healthy populations of fish and other organisms suggests that produced water discharges are not particularly toxic to aquatic life in the marine environment. A recently published risk assessment of produced water into shallow coastal waters (6) confirms this premise, concluding that ecological and health risks from radium in produced water appear to be small and that health risks from eating seafood contaminated by produced water discharges are negligible. Impacts to benthic organisms are possible within 200 feet of the discharge point, but no permanent damage to populations is expected.

Despite repeated attempts, investigators have had difficulty in determining the causative agents of toxicity in produced waters. Reference 7 presents data from a toxicity identification evaluation (TIE) on several produced waters. Observed toxicity could not be correlated with the presence of heavy metals, petroleum hydrocarbons, or BETX (benzene, toluene, xylene). Although the effluent tested in the study was hypersaline, reduction of the salinity did not eliminate toxicity. The authors concluded that the agents of toxicity could not be found.

The prevailing assumption in WET monitoring programs has been that observed toxicity always results from the presence of "toxic pollutants." Recent work, however, has shown that this is not always the case. The freshwater indicator organisms *Ceriodaphnia dubia*, a small invertebrate, and *Pimephales promelas*, the fathead minnow, can respond negatively to the presence of high quantities of dissolved solids, even when the ions present are not considered toxic per se but are, in fact, components of natural and synthetic freshwater (8). This so-called common ion toxicity or essential ion toxicity was discovered to be an important component of produced water toxicity to freshwater organisms. Although certainly the discharge of toxic effluents to receiving waters is not desirable, the nature of that toxicity is important to consider before making a determination of the potential long-term impacts of a discharge. Most current regulatory interpretations do not appear to account for essential ion toxicity.

The chemical makeup of produced water is important to consider when interpreting toxicity test results. Although produced waters from some parts of the country have salinities similar to or lower than those of seawater, most produced waters from the Gulf of Mexico are extremely high in dissolved solids, with salinities reaching 300 parts per thousand (ppt) or more (see Table 1). Toxicity testing organisms frequently used for monitoring effluent toxicity can withstand salinity up to only 50 ppt for only short periods of time. Test salinity is usually limited to 20-30 ppt. Although toxicity testing protocols offer assistance for increasing salinity of freshwater effluents slated for testing with marine organisms, no guidelines are provided for reducing salinity. If the salinity of an effluent can be raised to meet a test organism's tolerance range, it may also be appropriate to lower the salinity if it is above the organism's tolerance range.

Another important aspect of produced water is its ionic balance relative to seawater. Recent work, discussed in detail below, has demonstrated that toxicity testing organisms often have well-defined requirements and tolerances for at least some of the ions. Obviously, these "essential ions" are not pollutants in the classic sense, but they can and will cause toxicity if present in amounts differing greatly from amounts in natural seawater. Produced waters have extremely variable ionic compositions as illustrated in Table 1. Ionic balance should be considered when testing produced waters for toxicity.

EFFECTS OF SALINITY

Produced water may have a salinity as high as 300 ppt. The test organisms generally have a limited salinity tolerance range and are adversely affected if exposed to salinity outside their normal tolerance range. EPA's guidance document for conducting marine chronic toxicity tests (2) recommends culturing mysid shrimp, *Mysidopsis bahia*, at a salinity range of 30 ± 2 ppt, and at no less than 20 ppt if most tests will be conducted at a lower salinity. The EPA manual further recommends that to avoid unnecessary stress, organisms should not be subjected to changes of more than 2 ppt in salinity in any 24-hour period.

From the viewpoint of toxicity testing, the EPA has recommended two important tools. First, the salinity of effluent should be adjusted to match that of either the receiving water or the culture water for marine toxicity indicator organisms (2). Although this recommendation is relatively straightforward to implement for low salinity effluents, there is no method for salinity adjustment of hypersaline effluents that does not dilute other constituents. Second, the test organism should be acclimatized to the salinity at which the test is being conducted. To prevent salinity shock, the seawater should be adjusted by no more than 2 ppt per day. The acclimatization procedures work well at any salinity within the tolerance range of the test organism, except for hypersaline effluents.

We propose the following approach for toxicity tests in cases where the produced water salinity is greater than the tolerance range of the test organisms. If the salinity at the edge of the mixing zone falls within a range compatible with the salinity tolerance of the test organism, this concentration can be used as the highest tested concentration. Even a highly saline (300 ppt) produced water would require a dilution factor of only 10 at the edge of the mixing zone to bring the salinity into the tolerance range of the mysid shrimp. This should not be difficult to achieve for most offshore discharges. Because salinity is not, in itself, a pollutant, this strategy should be protective of the marine environment. This method will have the additional benefit of determining the potential impact of all other constituents in the discharge on the indicator organisms.

Another possible solution is to conduct tests with organisms that can withstand the high salinity. The brine shrimp, *Artemia fransisciana*, can withstand salinity as high as 300 ppt (3). This characteristic makes it a likely candidate for toxicity testing of produced waters. The organism is widely available and readily reared in the laboratory, making it an ideal toxicity testing organism. We are not aware of any researchers currently using *Artemia* in the testing of produced water toxicity.

ESSENTIAL ION BALANCE IN SEAWATER

Seawater is a complex mixture of more than 75 elements. While many marine organisms have evolved mechanisms to regulate their internal ionic chemistry, marine invertebrates simply maintain osmotic equilibrium with seawater. This makes them vulnerable to overt changes in the composition of their external environment. While this characteristic is the reason marine invertebrates are often used to monitor effluent toxicity (high sensitivity), it can also result in a toxic response to changes in the ionic balance of the seawater. Recent research has shown there are six essential ions required to support *Mysidopsis bahia*: Na, Cl, Ca, Mg, K, and Br (9). None of the other ions naturally present in seawater are required to support survival over the course of a typical toxicity test (96 hours). *Mysidopsis bahia* responds negatively to both excesses and deficiencies in these ions. In addition, the range of concentrations of each ion within which the organism survives (the tolerance range) changes as salinity changes. There may also be interactions among the ions with respect to survival of this organism. Additional researchers have also presented information regarding the determination of ion imbalance in produced waters and have developed a predictive model for the determination of ionic imbalance (10) in *M. bahia*, as well as two common fish indicator species: *Menidia beryllina* and *Cyprinodon variegatus*.

In a regulatory framework, the presence of toxicity caused by ion deficiency poses a serious interpretation problem. The regulatory guidelines are set up assuming that the presence of any compound is undesirable. This logic maintains that if the compound or element is removed, the resulting effluent quality is higher and toxicity is reduced. Although this logic is sound for the majority of pollutants, it fails to account for essential ions. Although most elements are toxic at some concentration, essential ions have two toxicity points, one of excess and one of deficiency. If one removes too many of them, the test organism dies. In a laboratory toxicity test, distilled and deionized waters are toxic, although no one would consider them pollutants.

The effects of an ion imbalance on survival of test organisms can best be visualized by example. Table 2 offers a number of case histories that illustrate ion imbalances caused by deficiency and excess. The first three examples are taken from reference 7; no attempt was made to correct an ionic imbalance. Although the presence of ion imbalance toxicity is probable, there is no way to prove that these samples would be nontoxic if they were balanced with respect to essential ions. When the last two effluents in the table, taken from reference 9, were subsequently corrected for an ionic imbalance, the observed toxicity was completely eliminated.

There are three ways to adjust a solution for ion balance, as outlined below. All three methods require analytical information on the solution being tested.

1) Deficiency: Add reagent-grade salts to bring the concentration up to the concentration found in natural seawater at test salinity.

2) Minor excess: Add reagent-grade sodium chloride to increase the salinity of the test solution. Be sure not to exceed the salinity tolerance of the test organism. Adjust the other essential ions as necessary to account for the increase in salinity.

3) Major excess: Remove excess ions with an ion exchange resin. Re-analyze the resulting solution and adjust ion deficiencies as required. Prepare and treat a "mock effluent" to confirm that a solution of essential ions of this type will be toxic and can be treated with ion balancing. This ensures that other toxins were not removed by the ion resin treatment.

These methods can all be successfully used to correct an ion imbalance in produced waters or other effluents being discharged to marine waters. However, the removal of toxicity is not sufficient to prove that ion imbalance is the sole cause of effluent toxicity. This is especially true when the third method is used, because of the potential for removal of other components of the effluent mixture. However, these methods can be used to screen effluents. If balancing the ions does not reduce toxicity, the toxicity is caused by some other component of the mixture. If balancing does reduce or eliminate toxicity, further investigative work, specifically the creation of "mock effluents," can help confirm that ionic imbalance is contributing to or causing the observed toxicity. This method has been used successfully to isolate calcium as an agent of toxicity in a petrochemical effluent (11). Methods for toxicity identification evaluations and mock effluents are provided by the EPA (12-15). In addition, the State of Florida has recently proposed guidelines for utilizing ion balancing techniques in WET testing (16).

The importance of this phenomenon is that although these ions can cause toxicity if present in large amounts, they are essential for survival in some amount and therefore cannot be considered pollutants. Certainly toxicity caused by a deficiency of essential ions cannot be considered pollution. When toxicity problems occur, permittees should check for an essential ion imbalance. If ionic imbalance appears to be responsible for the toxicity, on the basis of a TIE, regulators should be willing to review the data on a case-by-case basis. When proven, the location of the discharge, the nature of the ionic imbalance (excess or deficiency), and the amount of available dilution will need to be considered.

CONCLUSION

Produced waters will continue to require toxicity monitoring to ensure compliance with permit conditions. Certainly, some of these effluents may be

toxic as a result of the presence of something other than salinity and essential ion toxicity. These effluents may require treatment or other control to ensure protection of our marine resources. However, before any compliance decisions regarding a produced water discharge are made, the toxicity information generated must be carefully evaluated to ensure that unreasonable restrictions are not placed on the dischargers. The phenomenon of essential ion toxicity will continue to be examined, and our understanding of the effects of essential ions on toxicity test results will become more refined. Until that time, the following questions need to be answered for each effluent discharge:

1) Are any of the contaminants being measured likely to produce effects outside the mixing zone?

2) Is the effluent hypersaline, and is the salinity itself the primary toxicant? Although there are methods for directly answering this question, the easiest approach is to first dilute the effluent with clean seawater to the critical dilution, then assess toxicity. Alternatively, an indicator organism known to be tolerant to hypersalinity, such as the brine shrimp, can be used.

3) Are the essential ion requirements of the organisms being met in all test solutions below the critical dilution? Dilution of a hypersaline produced water may or may not produce a tolerable ion balance. Analysis of the test solutions, followed by comparison to known tolerance ranges and adjustment as necessary, will eliminate ion imbalance toxicity.

REFERENCES

1. "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Subcategory of the Oil and Gas Extraction Point Source Category," U.S. Environmental Protection Agency, EPA 821-R-93-003, January 1993.

2. "Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Water to Marine and Estuarine Organisms," 2nd edition, U.S. Environmental Protection Agency, EPA/600/4-91/003, July 1994.

3. "Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms," 4th edition, U.S. Environmental Protection Agency, EPA/600/4-90/027F, August 1993.

4. Stephenson, M.T., "A Survey of Produced Water Studies," in J.P. Ray and F.R. Englehardt (editors), *Produced Water: Technological/Environmental Issues and Solutions*, New York, Plenum Press, 1992.

5. "Characterization of Data Collected from the Louisiana Department of Environmental Quality Permit Files for Development of Texas and Louisiana Coastal Subcategory NPDES Permits," prepared for U.S. Environmental Protection Agency by Avanti Corporation, Vienna, VA, draft July 23, 1992.

6. Meinhold, A.F., M.P. DePhillips, and S. Holtzman, "Final Report: Risk Assessment for Produced Water Discharges to Louisiana Open Bays," prepared for U.S. Department of Energy by Brookhaven National Laboratory, Upton, NY, March 1996.

7. Schiff, K.C., D.J. Reish, J.W. Anderson, and S.M. Bay, "A Comparative Evaluation of Produced Water Toxicity," J.P. Ray and F.R. Englehardt (editors), *Produced Water: Technological/Environmental Solutions*, New York, Plenum Press, 1992.

8. Tietge, J.E., J.R. Hockett, and J.M. Evans, "Discrimination of Ion Toxicity in Six Produced Waters Using the Freshwater Salinity Toxicity Relationships and TIE Procedures," Society of Petroleum Engineers, SPE 29730, March 1995.

9. Douglas, W.S., and M.T. Horne, "The Interactive Effects of Essential Ions and Salinity on the Survival of Mysidopsis bahia in 96-Hour Acute Toxicity Tests of Effluents Discharged to Marine and Estuarine Receiving Waters," Environ. Toxicol Chem, *in press*.

10. Pillard, D.A., J.M. Evans, and D.L. DuFresne, "Acute Toxicity of Saline Produced Waters to Marine Organisms," Society of Petroleum Engineers, SPE 35845, June 1996.

11. Douglas, W.S., S.S. Grasso, D.G. Hutton, and K.R. Schroeder, "Ion Imbalance as a Source of Toxicity in an Estuarine Effluent," Arch. Environ. Contam. Toxicol, *in press*.

12. "Methods for Aquatic Toxicity Identification Evaluations: Phase II Toxicity Identification Procedures for Samples Exhibiting Acute and Chronic Toxicity," U.S. Environmental Protection Agency, EPA 600/R-92/080, September 1993.

13. "Methods for Aquatic Toxicity Identification Evaluations: Phase III Toxicity Confirmation Procedures for Samples Exhibiting Acute and Chronic Toxicity," U.S. Environmental Protection Agency, EPA-600/R-92/081, September 1993.

14. "Toxicity Identification Evaluation: Characterization of Chronically Toxic Effluents, Phase I," U.S. Environmental Protection Agency, EPA/600/6-91/005F, May 1992.

15. "Methods for Aquatic Toxicity Identification Evaluations: Phase I Toxicity Characterization Procedures," 2nd edition, U.S. Environmental Protection Agency, EPA-600/6-91/003, February 1991.

16. "Protocols for Determining Major-Seawater-Ion Toxicity in Membrane-Technology Water-Treatment Concentrate," Florida Department of Environmental Protection, December 1995.

17. Tibbetts, P.J.C., I.T. Buchanan, L.J. Gawel, and R. Large, "A Comprehensive Determination of Produced Water Composition," J.P. Ray and F.R. Engelhardt (editors), *Produced Water: Technological/Environmental Issues and Solutions*, New York, Plenum Press, 1992.

Table 1
Essential Ions in Seawater and Produced Water

Analyte	Seawater	Produced Water [1]	Tolerance Range [2]
Calcium (mg/l)	393 to 427	13 to 25,800	100 to 1,000
Magnesium (mg/l)	1,180 to 1,350	8 to 6,000	>0 to 2,000
Potassium (mg/l)	380 to 564	24 to 4,300	50 to 400
Bromide (mg/l)	65	unknown	5 to 700
Salinity (ppt)	34	~20 to 300	~10 to ~40

[1] From reference 17.
[2] For *Mysidopsis bahia* only, range varies with salinity; see text for details.

Table 2
Effect of Essential Ion Imbalance on *Mysidopsis bahia*

Analyte	PW I [1]	PW II [1]	PW III [1]	Effluent I [2]	Effluent II [2]	Seawater
Mg (mg/l)	220	80	270	294	1.5	1,350
K (mg/l)	170	136	63	71	12.4	380
Ca (mg/l)	1,060	760	741	2,370	4.2	400
Br (mg/l)	Nm [3]	Nm	Nm	5	5	65
Salinity (ppt)	30	30	30	25	25	34
Survival (%)	0	0	0	0	0	100

[1] From reference 7; following salinity adjustment; ion balancing not attempted.
[2] From reference 9; ion balancing removed toxicity.
[3] Nm = Not measured.

Achieving Common Sense Environmental Regulation: The Oil and Gas Exploration and Production Industry

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Abstract: The domestic oil and gas exploration and production industry produces 40 percent of the energy that powers the economy and fuels the quality of life Americans enjoy. The industry is committed to meeting America's energy needs while operating in an environmentally sound manner and protecting the health and safety of employees and the public.

It is important to achieve a balanced regulatory approach that protects the environment as well or better than the current system, and does the job more efficiently. Consideration of the costs and benefits of regulatory proposals, the use of risk assessment, compliance flexibility, decision-making based on sound science and rules that get something accomplished other than paperwork are *common sense goals*. These principles will help create a better balance allowing our nation to enjoy the benefits of domestic oil and gas production, as well as the economic activity it creates, without compromising environmental protection or the quality of life Americans have come to expect.

Many of the federal efforts now under consideration would cost a great deal while adding little additional environmental protection. Many federal programs duplicate existing state efforts to no apparent advantage. Many merely increase costly paperwork instead of achieving results. And many would limit industry flexibility and the adoption of new, better technologies as they are discovered.

On the other hand, common sense dictates that there is a better way. Common sense tells us that regulations should:

- be protective of the environment;
- be based on good science and the best possible data, and rely on the industry's expertise;
- be based on realistic analysis of risks so that the added environmental benefit from the program is clear;
- rely on cost-benefit analysis to produce a rational prioritization of problems to be addressed;
- be flexible and focus on performance, not methods, so that compliance can be achieved in the most cost-effective manner;
- not require unnecessary paperwork, needless monitoring or excessive permitting delays;
- recognize the uniqueness of the exploration and production sector of the oil and gas industry and the remoteness of most facilities; and
- build upon the success of existing state programs and industry practices.

Introduction

The domestic oil and gas exploration and production industry produces 40 percent of the energy that powers the economy and fuels the quality of life Americans enjoy. The industry is committed to meeting America's energy needs while operating in an environmentally sound manner and protecting the health and safety of employees and the public.

And much progress has been made. Working with state and federal regulators, in individual companies and jointly as an industry, the exploration and production industry is now more successful than ever before at locating and producing oil and gas with a minimum impact on the environment.

Because of these successes, regulators, the industry and the public need to take into account that future environmental progress will be harder to come by, and far more expensive. So we need to rely on environmental regulation that takes a more common sense approach than the traditional command-and-control methods used in the past. Consideration of the costs and benefits of regulatory proposals, the use of risk assessment, compliance flexibility, decision-making based on sound science and rules that get something accomplished other than paperwork are common sense goals. These principles will help create a better balance allowing our nation to enjoy the benefits of domestic oil and gas production, as well as the economic activity it creates, without compromising environmental protection or the quality of life Americans have come to expect.

The Development of State and Federal Environmental Regulation

Regulation to address these environmental issues is certainly not new, either at the federal or state levels. When the U.S. Congress enacted environmental legislation during the 1970s, it found that in most cases, the formation of a federal regulatory structure served as the primary model for states and localities that were just beginning to address environmental concerns. But that wasn't the case in the oil and natural gas exploration and production industry—the states had regulated the industry's impact on the environment for decades prior to federal regulation.

State environmental regulation. The states have been active in state environmental regulation for over 70 years. Oklahoma began regulation in 1916, Texas in 1919. Initially, these regulations dealt with production rates to curb waste of natural resources through overproduction and to protect the health and safety of the citizens.

These state regulatory structures were modified over time to address a wide range of environmental issues. For example, one of the earliest environmental regulations was the Texas Railroad Commission's Rule 20 issued in 1919. It stated that "Fresh water is to be protected. Fresh water, whether above or below the surface, shall be protected from pollution whether in drilling or plugging." As a result of this early start, when EPA began to implement the Underground Injection Control Program (UIC) of the Safe Drinking Water Act decades later, it discovered that many states, such as Texas, already had far more intricate and substantial UIC programs in place that dealt with the specific technical concerns of each state.

The Interstate Oil and Gas Compact Commission (IOGCC), an organization of the governors and state officials from the oil and gas producing states, with funding assistance from EPA and input from both environmental and industry groups, developed a model state oil and gas E&P environmental regulatory program. The published report in 1990 contained extensive technical and administrative criteria for E&P waste management programs based on site specific or regional differences in geology, hydrology, climate and waste characteristics.

To put these findings into practice, the IOGCC instituted a state-by-state review process that brought together state regulators, EPA, DOE, environmental groups and industry to take an in-depth look at how a state's existing regulations measured up to the model. Wyoming was the first state reviewed in 1991. In all, 14 states have completed the peer review process, two have completed follow-up reviews a few years after their initial review, and two other state reviews are underway.

Each state review serves as a means of identifying methods for improving regulatory programs. The process provides experts from outside the state to look inside individual programs—not with an eye toward leveling criticism, but rather to offer constructive recommendations. These recommendations are not binding on the state, but offer a blueprint for change to be considered by state legislators and regulators. This highly successful program was cited by President Clinton's State-Federal Technology Partnership Task Force as a model for developing highly successful and efficient state-federal partnerships.

Federal environmental regulation. Since the 1970s the federal government has added another layer of environmental statutes and regulations in many areas. In 1969 Congress passed the National Environmental Policy Act and by the end of 1970, the Clean Air Act was passed. In the next ten years, Congress passed eight other major environmental laws: the Clean Water Act; the Federal Insecticide, Fungicide and Rodenticide Act; the Marine Protection, Research and Sanctuaries Act; the Endangered Species Act; the Safe Drinking Water Act; the Toxic Substances Control Act; the Resource Conservation and Recovery Act; and the Comprehensive Environmental Response, Compensation and Liability Act (better known as Superfund). In 1986 the Emergency Planning and Community Right-to-Know Act became part of Superfund, and in 1990 the Clean Air Act Amendments and the Oil Pollution Act were passed.

Achieving Further Environmental Progress: Common Sense Regulation of the Exploration and Production Industry

With such extensive state and federal environmental regulation of the oil and natural gas exploration and production industry already in place, experience bears out the obvious: significant environmental gains have already been made. E&P operations—and their environmental impact—are worlds away from the first well drilled in 1859.

The logical question is, where do we—industry and regulators—go from here? How much cleaner can, and should, the industry become—and how much are Americans willing to pay for marginal progress? And how can all of us—industry, regulators and the public—ensure that the course chosen buys the most environmental progress for the money?

These are timely questions. Continuing many of the federal efforts as proposed would cost a great deal while adding little additional environmental protection. Many of the federal programs duplicate existing state efforts to no apparent advantage. Many of the federal programs merely increase costly paperwork instead of achieving results. And many of the federal programs limit industry flexibility and the adoption of new, better technologies as they are discovered. Indeed for little if any environmental gain we could see the quality of life in some states actually decline as their economies are weakened.

On the other hand, common sense dictates that there is a better way. Common sense tells us that regulations should:

- be protective of the environment;
- be based on good science and the best possible data, and rely on the industry's expertise;
- be based on realistic analysis of risks so that the added environmental benefit from the program is clear;

- rely on cost-benefit analysis to produce a rational prioritization of problems to be addressed;
- be flexible and focus on performance goals, not methods, so that compliance can be achieved in the most cost-effective manner;
- not require unnecessary paperwork, needless monitoring or excessive permitting delays;
- recognize the uniqueness of the exploration and production sector of the oil and gas industry and the remoteness of most facilities; and
- build upon the success of existing state programs and industry practices.

Do Federal Regulations Currently Under Discussion Pass The Common Sense Test?

Unfortunately, many of the federal regulatory efforts now underway do not pass a simple "common sense" test. In many cases, the proposals under discussion have been formulated without reliance on the years of expertise in the states and without regard to the unique nature of the exploration and production industry—rather, they are merely applications of manufacturing processing methods to the E&P industry. The proposals often start with a method for addressing an issue, not with an appropriate environmental goal.

Here is an analysis of some of the major federal regulatory efforts now underway that will apply to the exploration and production industry if implemented. Here's why each of these fails a "common sense" test, followed by a recommendation for a better way to address each issue.

Expansion of the Toxics Release Inventory Program.

The Toxics Release Inventory (TRI) program was created by the Emergency Planning and Community Right to Know Act of 1986 (EPCRA) , also known as Title III of the Superfund Amendments and Reauthorization Act (SARA/Title III), to provide communities with information on manufacturing activities. Companies in manufacturing industries are required to file toxic release reports. These contain inventories of the estimated releases to air, water and land from the manufacturers' operations of any of 648 chemicals.

In June 1994, the Environmental Protection Agency published a notice of proposed rulemaking to add seven non-manufacturing industries to the TRI reporting program. EPA is still considering whether to issue an advanced notice of proposed rulemaking to extend the TRI to the exploration and production industry.

The inclusion of oil and natural gas exploration and production facilities in the TRI program would require companies to report annually on the amounts of each listed chemical "released" by a facility into the environment, either from routine operations or as a result of accidents, and the amounts of wastes that undergo recycling, energy recovery, and treatment. There are major problems with this proposal that have caused the industry to conclude that this is a misdirected effort. For example, E&P streams could require extensive testing and reporting on the constituents of the produced water which are disposed of into underground injection wells. There is little or no exposure to the public from these "releases."

For example, in October 1994 an article in the *Bakersfield Californian* carried a headline billing DOE's Elk Hills field as Kern County's top polluter. The conclusion drawn by the newspaper from the government data was erroneous because over 99 percent of the reported "releases" consisted of TRI chemicals that were injected into the original hydrocarbon reservoir, not released to the environment. Clearly, this type of misleading information provides no benefit to the community, or to the environment.

And yet, the cost of compliance with this paperwork reporting requirement would be extremely high. TRI compliance costs could exceed $200 million in the first year and $100 million each year after that. This program would only divert industry resources from sensible pollution prevention efforts and state programs that could satisfy the community's right-to-know desires in a more meaningful way.

This proposal *fails* the *common sense* test because it does not recognize the unique nature of the E&P facilities, it requires useless paperwork, its estimated costs far outweigh the estimated environmental benefits, it isn't based on a realistic assessment of risks, and it duplicates existing state and/or other federal regulations.

Solution: The exploration and production industry supports pollution prevention and providing information that has value to local communities. Any additional information needed by the public, beyond that which is currently reported under existing state and federal regulations, should be addressed through existing information channels at the state level. EPA has already funded the Interstate Oil and Gas Compact Commission's state review program to improve state regulatory programs through cooperative efforts and peer review among the states and their federal and industry partners.

Production Wastes

Most exploration and production wastes are currently managed under state regulatory programs and are exempt from the hazardous waste management requirements of the federal Resource Conservation and Recovery Act (RCRA). Continued jurisdiction over E&P wastes at the state level was supported by EPA after an extensive investigation concluded in 1988 with the issuance of a "regulatory determination" in the Federal Register confirming the low toxicity of E&P wastes. However, in May, 1995 the EPA Office of Solid Waste (OSW) released for comment a series of technical resource documents on three E&P associated wastes categories. The OSW used the Toxicity Characteristic Leaching Procedure (TCLP) model to rank the hazard potential of these three associated wastes and the management practices used to dispose of them. The TCLP is not the appropriate land disposal model for determining this ranking.

The TCLP estimates the potential hazard from a stream based on the assumption of a steady and continuous leaching process, as would occur at a large sanitary landfill. However, E&P associated wastes are largely hydrocarbons and are disposed in most cases on the land surface. They are spread once at the site, mixed with soil and fertilized to enhance biodegradation mechanisms. The leaching of the waste/soil mix onsite has little or no impact on ground water, because the hydrocarbons are metabolized and not available for leaching. As a result, the TCLP model in most cases overstates the hazard potential of E&P associated wastes, because it was not designed specifically to simulate E&P waste management processes.

In the technical documents, EPA's conclusions were critical of existing state solid waste management programs. EPA is revising the documents for release in 1996. If they are still based on TCLP rankings of hazard potential, the revised documents could place pressure on state agencies to unnecessarily modify or discontinue certain E&P waste management practices. Costs would be increased significantly, but with little or no environmental benefit.

Use of the TCLP to evaluate E&P wastes *fails* the *common sense* test because it is not an appropriate model for assessing the hazard potential of E&P wastes.

Solution: EPA should use another model for determining the hazard potential of E&P associated wastes before recommending changes in industry practices and state regulatory methods. The industry believes that the land disposal model, VADSAT, more accurately estimates the ground water impact from land disposing associated wastes than the TCLP model. VADSAT was designed specifically to evaluate industry's current land-based

waste management practices and simulate most of the processes that naturally degrade and attenuate associated wastes in the environment.

"MACT" Air Emission Controls

The Clean Air Act Amendments of 1990 require that companies adopt the "Maximum Achievable Control Technology," or "MACT," on facilities that are major sources of hazardous air pollutants (HAPs). To implement this law, the Environmental Protection Agency (EPA) is expected to propose new air emission controls for the oil and natural gas production source category in 1997 and to publish a final rule one year later. These new regulations will require production operations to install "MACT" if equipment emits greater than threshold levels of HAPs, such as benzene and n-hexane.

EPA's draft document titled "Oil and Natural Gas Production—Background Information for Proposed Air Emission Standards" contains technical information and analyses describing how EPA plans to develop emissions controls for the exploration and production industry. EPA is using emissions data collected from 25 oil and gas companies to propose MACT standards for E&P. The data is being used to: develop "model plants" for various E&P facilities, such as glycol dehydrators, tank batteries and gas plants; estimate the total number of E&P facilities in the United States; estimate national emission of HAPs from the industry; and specify controls and monitoring requirements for E&P.

The Clean Air Act requires EPA to develop control standards for existing E&P equipment to be controlled by the rule based on the average performance of the best 12 percent of existing sources in the industry—known as the MACT "floor"—and the cost of controls cannot be considered in making this determination. EPA can also propose more stringent controls than this floor if the Agency can show that the controls are cost effective. Controls will be required on "major sources," those with the potential to emit 10 tons of any single HAP or 25 tons of a combination of HAPs in a year. Additionally, EPA plans to propose controls on non-major ("area") sources (for example, glycol dehydrators with emissions below the major source thresholds) which EPA determines present a risk warranting regulation. These controls may be based on less stringent "generally available control technology."

Over the past three years EPA has developed national emission estimates for E&P facilities and proposed controls for glycol dehydrators, tanks, and natural gas processing plants. But EPA's data is not representative of E&P operations, or the emission controls currently in place.

This draft proposal *fails* the *common sense* test because it relies on very limited data, its estimated costs far outweigh the estimated environmental benefits, and it doesn't recognize the unique nature of E&P facilities.

Solution: API has formally objected to EPA's initial draft proposal and has asked the Agency to work with industry to correct major flaws. These initial flaws stem from the overestimation of HAP emissions from the industry. EPA and the industry are endeavoring to resolve major concerns with the initial draft proposal, and a formal proposal is expected in early 1997.

Spill Prevention, Control, and Countermeasure Plans

In January, 1988 a four-million gallon aboveground transportation-related storage tank collapsed and approximately 750,000 gallons of diesel fuel were released into the Monongahela River. As a result of this tragic accident EPA proposed a revision to Spill Prevention, Control, and Countermeasure Plan (SPCC) rule in October, 1991.

The proposed regulations (Phase I) will require all tank batteries near "navigable" waters (as defined by the Clean Water Act) to prepare and certify additional plans for preventing or controlling a spill of tank contents. But the small size of most tanks associated with exploration and production make the potential damage minimal in the event of a spill. Moreover, most E&P tanks are already constructed with dikes, berms, or other protective measures to contain any spilled material and prevent it from reaching surface water.

The proposed regulations were an overreaction to an isolated incident, and did not take into consideration the effectiveness of existing state and federal requirements. Onerous provisions such as unreasonable secondary containment, implementation schedules, mandatory language, and inspection frequencies should be revisited based on factual information about the effectiveness of existing tank systems.

The final rule has been delayed pending a review ordered by the Office of Management and Budget of the cost effectiveness of the proposed regulations. EPA estimated first-year costs to be $9.9 million and per year costs of $200,000 to implement the rule. Other studies, however, estimate annualized costs of $145 million, with changes to facilities' drainage system design potentially adding another $128 million in costs.

Not only does a substantial difference in opinion exist as to the cost of the proposal, but the benefits of more stringent federal regulations have not been adequately justified. A task force of EPA, other agency, and state officials, called the SPCC Task Force, reviewed OMB's concerns and recommended changes in the regulations. They also found that "EPA does not have an adequate inventory of facilities subject to the regulations and recommended that EPA gather specific information about these facilities." A report by the General Accounting Office made similar recommendations.

This proposal *fails* the *common sense* test because it duplicates existing state and/or federal regulations, it limits industry flexibility and the adoption of new, better approaches, its estimated costs far outweigh the estimated environmental benefits.

Solution: EPA should gather the specific information recommended by the SPCC Task Force about facilities currently regulated before proposing new regulations. A common sense approach to rulemaking should be employed which recognizes the effectiveness of existing programs and analyzes the costs and benefits of more stringent regulations. One failure, serious though it was, should not be used as the sole justification for a wide-reaching federal regulatory program that is duplicative of current state and federal requirements and will not produce any additional environmental benefits.

"Best Management Practices" Plans

The Environmental Protection Agency's Region X office has proposed that a "Best Management Practices" (BMP) plan for produced water and drilling wastes be required in the drilling and production permit for Cook Inlet off Alaska. A BMP is a practice designed to prevent or reduce water pollution, as for example, when bales of hay are used to block runoff from construction sites.
EPA's headquarters in Washington considered the need for BMPs in both the Coastal and Offshore Guidelines and decided that they should not be required. In fact, under the Clean Water Act, authority to require the plans only exists when hazardous substances other than oil could significantly pollute navigable waterways. In commenting on the final language of the Clean Water Act in 1977 the conference committee stated that EPA is not authorized "to become involved in actual plant process design and operating decisions."

Yet EPA's Region X has proposed that in Cook Inlet "the number and quantity of pollutants and the toxicity of effluent generated, discharged or potentially discharged at the facility shall be minimized by the Permittee to the extent feasible by managing each effluent waste stream in the most appropriate manner." Plans requiring continual reductions, as proposed here, could mean that an operation will have to move toward zero

discharge—no discharge of drilling wastes or produced water—or face the possibility that a concerned citizen could initiate an enforcement action if they believed that pollutants were not being minimized to the extent feasible.

The cost of zero discharge for produced water would be an initial capital cost of almost $85 million and an operating cost of $9.5 million per year for Cook Inlet. Zero discharge of drilling wastes—mud and cuttings—would cost $3.9 million per year. The EPA has already rejected zero discharge in the 1993 Offshore Effluent Guidelines as not being cost effective.

This proposal *fails* the *common sense* test because it requires useless paperwork, needless monitoring or excessive permitting delays, it duplicates existing state and/or other federal regulations, it limits industry flexibility and the adoption of new, better approaches, its estimated costs far outweigh the estimated environmental benefits.

Solution: Requiring Best Management Practices plans for permits in Cook Inlet would exceed EPA Region X's statutory authority. BMPs should only be required if substances other than oil that are hazardous pollutants can be present in significant amounts in waste streams, as clearly intended by the Congress.

Naturally Occurring Radioactive Materials

Industry and regulators have been aware of the presence of naturally-occurring low level radioactivity in some oil and gas producing and processing operations for some years. Small amounts of Naturally Occurring Radioactive Material (NORM) have been found in scales, sand, sludges and films deposited in tubing and surface equipment used in drilling and production. In addition, some deposits have been found in soil from past disposal practices.

A number of scientific studies have demonstrated that the low concentrations of NORM typically found at oil and gas E&P sites present little risk to humans. Moreover, E&P sites are generally remotely located and present little or no chance for exposure to the general public. However, because potential risks could exist if NORM is present in significant concentrations, the industry and state regulators have incorporated these concerns into waste management practices. Several states have developed standards to protect workers and the public from any risks posed by these wastes.

But despite current waste management practices and state regulation addressing these concerns, EPA appears to be planning to revise federal guidance which would, for the first time, incorporate NORM into its scope. The updated Radiation Protection Guidance for the General Public, expected to be issued in 1996, could set unrealistically low radiation limits. Many sites which satisfy state rules may not meet the proposed criteria and could potentially become targets for remediation. Based on analyses released by EPA, it has been assumed that under federal NORM regulations all oil and gas sites would be required to be decontaminated prior to abandonment to less than 5 picocuries per gram of radionuclides—a level that may be too low to even be measured reliably. In addition, special handling and control of equipment and materials containing NORM could be required if measurements exceed 15 millirem per year from an oil and gas production facility.

This can be compared to natural background radiation we're exposed to all the time of about 300 millirems per year. About 100 millirems of this is from breathing radon gas while the other 200 millirems comes from what we eat and drink, cosmic rays, the soil, building materials and various medical procedures. Fifteen millirems per year is less than the radiation emitted from a typical granite or marble building—buildings such as Grand Central Station in New York and the Capitol in Washington, D.C. give exposures in excess of 100 millirems annually.

The potential federal regulation of NORM could add new costs to industry practices with very little, if any, reduction in human health risks. The costs to the exploration and production industry have been estimated at $136 million initially and $246 million each year thereafter. Costs would vary, however, depending on the site remediation criteria selected and whether operators can wait to clean up until after a site is closed. On the benefits side, remediation to the proposed limits only reduces the hypothetical risk of cancer if you assume that closed sites will be used for residential housing after remediation.

This proposal *fails* the *common sense* test because it duplicates existing state and/or other federal regulations, it limits industry flexibility and the adoption of new, better approaches, its estimated costs far outweigh the estimated environmental benefits, it is not based on a realistic assessment of risks.

Solution: Regulation of NORM in the oil and gas industry should be left to the states. For the vast majority of sites, the intended uses of the land after remediation are such that the public would not gain any additional benefits from the application of EPA's anticipated radiation site clean-up requirements to sites containing NORM.

Existing Federal Regulations Can Be Made Better With Common Sense

In addition to resolving the pending issues in a common sense manner, the industry believes existing regulatory policy can be changed to provide win-win successes: competitive, low-cost energy for society produced in a way that protects the environment and human safety. Here are proposals that *pass* the common sense test.

Underground Injection Control

The Environmental Protection Agency regulates oil- and gas-related (Class II) injection wells, used by the industry to increase oil and gas production and to dispose of produced water—generally briny water brought to the surface during oil and gas production. In reviews in both 1982 and 1987, EPA—specifically the Office of Ground Water and Drinking Water in Washington—identified the waste fluids "qualified" for injection into these wells.

In 1982, EPA modified the list of waste fluids to include waste water at gas plants, regardless of its source. In 1987, the list was again reviewed and the list was expanded to include scrubber liquids, softener regeneration brines and certain freshwater streams. These changes were adopted nationwide.

However, the national list of qualified fluids has not been updated since 1987. In 1993, EPA's Region VI office broadened the list to include RCRA E&P exempt wastes as defined by the EPA Office of Solid Wastes since these wastes are non-hazardous and are integrally associated with oil and gas operations or storage activities. Also in 1993, the EPA Office of Ground Water and Drinking Water prepared draft guidance to include E&P exempt wastes on the nationwide list, but the statement was never issued.

Updated guidance would provide regulatory consistency, protect the environment and would also significantly reduce the industry's costs relative to other disposal options. The injection of all types of non-hazardous fluids associated with oil and gas industry operations or storage activities will not increase risk to drinking water supplies, as evidenced by EPA Region VI actions taken in 1993.

Solution: EPA's Washington Office of Ground Water and Drinking Water should issue guidance allowing the injection of all non-hazardous waste fluids integrally associated with oil and gas operations and storage activities into Class II UIC wells.

This proposal *passes* the *common sense* test because it improves industry flexibility and encourages the adoption of new, better approaches, and it would reduce industry costs without reducing environmental benefits.

Emergency Planning and Community Right-to-Know

Congress responded to the Bhopal disaster in India by enacting into law the Emergency Planning and Community Right to Know Act (EPCRA), also known as Title III of the Superfund Amendments and Reauthorization Act (SARA/Title III), in 1986. The purpose of Sections 311 and 312 of this law was to require companies that operate facilities using large amounts of hazardous chemicals, such as chemical plants and refineries, to notify state and local emergency planners and emergency personnel like the local fire department of the quantities and types of hazardous chemicals they use and produce. Under this program, companies notify local and state officials when the chemicals are first used onsite and then file annual inventory information.

Although the exploration and production industry was not initially included in this program designed for large, centralized facilities, in 1987 the expansion of the related Occupational Safety and Health Administration Hazard Communication program triggered an expansion of Sections 311 and 312, requiring that many small operations like exploration and production facilities begin to file reports.

From the beginning EPA correctly recognized that exploration and production activities were unique, allowing companies to file reports on chemical categories instead of trying to identify and assess each individual chemical product. Companies also were allowed to file one report to represent more than one facility if the facilities were essentially the same.

However, eight years of compliance experience, even with the modified filing methods allowed by EPA, have shown that the program is heavy on paperwork without providing community leaders with any real, usable information on potential problems the facility might have. In most cases, the program requires each operator to file repetitious reports each year of the same information. These reports, which can easily be inches thick, are provided to the local fire department, county or area planning agencies and state commissions. Current law makes the assumption that the receipt of these stacks of paper actually increases the community's understanding of the facility and how to respond in an emergency. That is simply not the case.

Solution: A more common sense approach would be to modify the reporting program for the exploration and production industry, making the program more effective for everyone while reducing the paperwork. Reporting requirements could be reduced while maintaining essential information, including:

- A one-time filing of a comprehensive list of chemical categories that could be present at some point during the life of the facility;
- Identification of the chemical categories that may be stored onsite longer than twelve months, with certified maximum volumes;
- A notice that material safety data sheets are available upon request; and,
- Emergency contact information, updated as necessary.

This level of reporting would provide usable information and complement many existing, voluntary emergency planning efforts which companies already undertake for facilities that pose a potential risk. A modified

reporting program, combined with industry efforts already underway, would provide communities with real knowledge and the ability to respond in the unlikely event of an exploration and production accident. Removing an unnecessary paperwork regime—originally designed for refineries and large chemical plants—would give company officials more time for these meaningful activities.

This proposal *passes* the *common sense* test because it eliminates useless paperwork, it recognizes the nature of E&P facilities, it improves industry flexibility and encourages the adoption of new, better approaches, and it reduces industry costs without reducing environmental benefits.

Oil Spill Reporting

The Clean Water Act prohibits the discharge of "harmful quantities" of oil into navigable waters. And in 1978 Congress modified the harmful quantity criteria of Section 311 by changing the wording from quantities of oil that "will be harmful" to quantities that "may be harmful." EPA regulations have defined the term "harmful quantities" to apply to all discharges which "violate applicable water quality standards or cause a film or sheen on or upon the surface of the water...."

Since virtually all discharges of oil will cause a sheen, under current regulations virtually all discharges are considered to be "a harmful quantity" and therefore subject to the reporting and enforcement actions of the Clean Water Act. In 1985 EPA considered a petition to replace the sheen test with the measurable quantity of one barrel, but the Agency rejected it "in view of the successful and effective implementation of the existing oil sheen test over the past 14 years and the Agency's continued confidence in that procedure, and because the Agency at the moment has insufficient information on which to establish an alternative test that would meet the statutory based criteria of environmental protection and assure reliability and ease and consistency in implementation and enforcement."

The legislative and regulatory history of oil spill reporting points to a lack of scientific rationale in determining the harmful quantity criteria. Other laws have been far less arbitrary. For example, the statute implementing the Superfund program requires the EPA to establish "reportable quantities" of hazardous substances. Although petroleum and natural gas were specifically excluded from the definition of hazardous substances, for other hazardous substances EPA establishes a reportable quantity based on the effects on human health and the environment. This is a far more sensible approach than requiring reporting of any amount which "causes a sheen."

According to Coast Guard records approximately 8,000 oil spills were reported in 1994, and in three-quarters of these less than 10 gallons were spilled. Eliminating reporting and fines (about $500 each) for spills of less than 10 gallons could reduce administrative costs by an estimated $4.8 million per year. Some smaller threshold would reduce costs as well, but by a lesser amount.

Solution: The reportable quantity for oil spills should be based on its harmful characteristics and assessed as a quantitative amount in pounds. This would substantially reduce the number of spills that need to be reported without losing the benefits of having the truly "harmful" spills reported.

This industry proposal *passes* the *common sense* test because it eliminates useless paperwork, and it would reduce industry costs without reducing environmental benefits.

Offshore National Pollutant Discharge Elimination System (NPDES) Permits: Making the Permit System More Efficient

Under a program established by Section 402 of the Clean Water Act, the Environmental Protection Agency establishes limits on the amounts of certain pollutants that can be discharged by municipal sewage treatment plants and industrial facilities. These "effluent limits" are incorporated into National Pollutant Discharge Elimination System (NPDES) permits issued to municipal and industrial facilities that discharge water. Under the Clean Water Act, it is illegal for dischargers to operate either without a permit or in violation of permit conditions.

But the NPDES permit system doesn't operate as efficiently as it could. Businesses whose operations depend on having current permits would like to see improvements in the current system. These changes would help ensure that law-abiding, environmentally-concerned companies are able to receive the permits they need to operate in a timely fashion, while allowing regulators to use their resources to greater effect elsewhere.

Solution

Here are some suggestions:

- The industry would like to work with EPA to develop a generic NPDES individual permit application form specific to E&P operations that could be used in place of EPA Form 2C—saving the industry and EPA from a costly paperwork burden. Currently, applications for individual NPDES permits must be submitted on EPA Form 2C—a form that applies to any discharger. As a result, the form requires applicants to complete more than eight pages of data elements that are insignificant if not irrelevant to regulating E&P operations. There is no value-added to EPA from this additional data, yet the Agency will not process the application unless it is completely filled in. A form specific to E&P industry facilities would save both the industry and regulators time and money without lessening the environmental benefits of the program. Further, EPA rarely processes individual permit applications for E&P activities because they claim a lack of staff.

- NPDES permits should be issued in a more timely manner. Currently, permit issue and reissue delays cause disruptions in oil and natural gas operations at great expense to operators who must delay drilling and development operations until permits are issued. The EPA asserts that resources—mainly permit writers—are limited and that other programs take priority.

  But lengthy delays place operators in an untenable position . They either must absorb the financial burden of leases which can't be operated, and the United States must increase oil and gas imports and lose royalties on these leases, or the operators must absorb the added cost (of at least $1 million per well) of no-discharge wells and the increased risk of inadvertent discharges.
  The industry would like to see EPA establish a program that would allow third-party contractors to prepare the permit on an expedited basis, at the option and expense of permit applicants. EPA would administer the program, monitor the contractor and issue the permit, retaining their authority over NPDES permits and ensuring the integrity of the program. And the Agency would probably save money by adopting this proposal, as applicants would pay for the cost of timely permit processing.

- The industry would like to work with EPA to extend coverage of expired permits to operations that weren't covered prior to the permit's expiration. Once a general NPDES permit has expired, operators are unable to get permit coverage for new leases until a new permit is issued. And, as mentioned above, lengthy delays are commonplace, especially in reissuing expired permits, as has been the case with territorial seas permits which expired in 1984. Operators that were not covered for a particular lease when the permit expired must

either spend the additional funds for a "no discharge" project or defer the project for years, literally decades in some instances.

- Another way to relieve the industry's problems stemming from EPA's slow handling of reissuing expired permits would be to extend the permit term to 10 years. Currently, permits are issued for five years, then expire and must be renewed. In many cases, EPA has spent more time working on a permit than the time actually covered by the permit. The industry suggests that extending the length of the permit to ten years would place less of a burden on EPA's scarce resources while providing operators with more predictability on permit terms, conditions and coverage.

- In the Gulf of Mexico, E&P operators must comply with various NPDES permits, and the industry believes that compliance—and environmental benefits—would be increased if they were consolidated to the extent feasible. EPA has issued NPDES general permits for:

  - the Eastern Gulf of Mexico OCS (currently expired),
  - Central and Western Gulf of Mexico OCS,
  - the territorial seas of Texas,
  - the territorial seas of Louisiana,
  - coastal Louisiana for produced water and sand,
  - coastal Texas for produced water and sand,
  - coastal Louisiana for drilling and other discharges, and
  - coastal Texas for drilling and other discharges.
  - And, EPA Region IV is considering issuing a general permit for the Eastern Gulf of Mexico and then requiring individual permits for each lease block on which drilling activity will take place.

  Each permit has its own effluent limitations depending on when it was last issued, each permit has differing sampling and record keeping requirements, and each expires on a different day. The industry recommends consolidating these permits as much as possible to minimize confusion and improve compliance. Operating personnel routinely travel from one permit area to another to perform similar work, and despite frequent training, problems continue to occur as a result of the confusion surrounding permit conditions on any particular day in any particular location. While permits will differ according to local conditions, bringing some consistency into the process would improve compliance.

- Inconsistencies also exist among the two EPA Regions, VI and IV, responsible for E&P discharges into the Gulf of Mexico. The industry recommends that EPA place regulatory control of all E&P discharges in the Gulf of Mexico under Region VI, since they have the experience base to make decisions without revisiting issues that have been resolved. Region VI has roughly two decades of experience with E&P discharges and their environmental effects. Region IV has less experience with E&P facilities, and as a result, is requiring costly data gathering and monitoring to address questions previously answered for Region VI. For example, biomonitoring studies can easily add $100,000 to the cost of a single well drilling project, and more comprehensive studies can cost as much as $3 million. This duplication of effort doesn't make sense.

These proposals *pass* the *common sense* test because they eliminate useless paperwork, needless monitoring and excessive permitting delays, they reduce industry costs without reducing environmental benefits, it allows industry flexibility and the adoption of new, better approaches, and it reduces duplication among state and/or federal regulations.

Offshore National Pollutant Discharge Elimination System (NPDES) Permits: Partnership for Enhanced Compliance

The current method of enforcement creates barriers to communication between the EPA and the regulated community—E&P operators. This climate has a stifling effect on achieving full compliance because it has generated attitudes in the regulated community which range from distrust to extreme paranoia.

Many EPA enforcement personnel are unfamiliar with E&P personnel, facilities and operations. This tends to make the EPA skeptical and distrustful of the industry. And when EPA is called upon by operators to render judgments on regulatory interpretations, the situation is often poorly described and key data not presented. Rulings based on incomplete information or understanding add unnecessary costs without achieving environmental benefits and perpetuate misunderstandings, confusion and mistrust between operators and regulators. This situation doesn't benefit anyone.

Solution: EPA and the industry should take steps to build a cooperative approach that would maximize compliance within the E&P industry. Proposals include:

- A cooperative compliance assurance program could be developed that would encourage operators to invite EPA to inspect E&P facilities with the intent of helping the regulated community achieve full compliance without fear of fines and penalties. This type of program would eliminate barriers to communication by sharing industry and regulator experience on personnel, facilities, operations and waste streams. In addition, operators would gain a higher level of understanding and training on EPA's compliance goals.

- EPA should have the discretion to not fine operators for self reported violations where the operators continue to place a priority on and demonstrate good compliance programs, training programs and a desire to comply with the permits. Current fines create a disincentive for self-reported violations, creating a competitive disadvantage for operators who are diligent about reporting violations versus those who are not. EPA has stated that it is its belief and experience that not all operators report violations with the same degree of scrutiny. A better system would not make the diligent operator reporting all violations take the heat of both enforcement fines and public consternation while those not reporting can escape notice.

- EPA enforcement personnel are unwilling to visit offshore facilities, especially those undergoing enforcement actions, due to the travel costs incurred by the operator and EPA's concern that this might be a "conflict of interest." However, EPA enforcement personnel have expressed the belief that the opportunity for such visits would improve their ability to learn about the industry and to make better decisions. Operators would like the option of transporting EPA enforcement agents to any affected offshore facilities so that EPA can have as true an understanding of the facts as possible.

These proposals *pass* the *common sense* test because they improve industry flexibility and encourage the adoption of new, better approaches, they recognize that more can be accomplished if industry and regulators combine their expertise than in an adversarial climate, and they recognize the unique nature of E&P facilities.

Offshore National Pollutant Discharge Elimination System (NPDES) Permits: Flexibility is Needed

EPA regulations and permit systems should be flexible enough to recognize that E&P operating conditions vary from site to site. For example, current policy is that effluents authorized in an NPDES permit are authorized for discharge, and conversely, effluents not specifically identified are not authorized for discharge. It is not uncommon for operators to recognize routine effluents not captured by the permit despite diligence on the part of EPA and operators to identify all potential effluents before the permit is issued. Yet the EPA permit

modification process is cumbersome and time consuming, and EPA has been reluctant to modify permits unless forced to do so through litigation initiated by the operator.

Another example is the impact of dissolved oil which varies from site to site. Dissolved oil was the main issue raised by API in the Offshore Guidelines litigation before the Sixth Circuit Federal Court of Appeals. API showed that EPA had assumed that compliance with its Clean Water Act regulations could be achieved for all locations by improved operations and maintenance, when the data used by EPA showed that 10 of 52 platforms could not meet the produced water oil and grease limits of 29/42 mg/l without expensive modifications. These locations can meet the standards, but at least one is injecting produced water and others are taking extraordinary processing and treating measures to meet the limits. The industry is concerned about future deepwater development where, in some instances, oil characteristics could result in higher dissolved oil levels in produced water. Site specific variances would allow EPA to minimize dissolved oil discharges while recognizing that facilities face differing conditions.

A similar problem occurs when sanitary waste effluent limits designed to mesh with state effluent guidelines are imposed on platform facilities, without regard to their remote location and engineering practicalities. Most operators treat sanitary waste with self-contained treatment units designed for use on vessels and certified by the U.S. Coast Guard as Type II MSDs. But the strict Total Suspended Solids (TSS) and Biochemical Oxygen Demand (BOD) tests preferred by EPA for their consistency with onshore facilities has resulted in inconsistent and unreliable results. Consequently, exceedance of sanitary waste effluent limits is one of the most common areas of NPDES permit violations for oil and gas operators.

Solutions: More flexibility should be included in EPA's regulatory system. Proposals include:

- The NPDES permits should be changed to recognize that existing effluents are authorized unless specifically identified, regulated and or prohibited by the permit.

- EPA should establish a policy to grant a Fundamentally Different Factor (FDF) variance for locations that demonstrate concentrations of dissolved oil above the compliance limits.

- A sanitary waste effluent limitation based on residual chlorine level should be adopted for oil and gas facilities. Use of a residual chlorine limitation is consistent with the certification requirements for a Type II MSD and ensure that the effluent is properly disinfected.

These proposals *pass* the *common sense* test because they recognize the unique nature of E&P facilities, they improve industry flexibility and encourage the adoption of new, better approaches, they recognize that more can be accomplished if industry and regulators combine their expertise than in an adversarial climate, and they reduce useless paperwork, needless monitoring or excessive permitting delays.

Synthetic Drilling Muds

Efficient drilling technology is essential to meet the needs of the oil and gas industry. Both the challenges of new oil and gas provinces, especially in offshore waters, and the demands for effective environmental protection have driven the development of new technology. A key factor influencing drilling technology is the drilling fluid or mud used in drilling operations. New oil industry developments facilitated by improved drilling fluids technology include horizontal and extended reach drilling, as well as drilling in frontier areas and to increased depths. Such capabilities and conditions demand careful attention to the selection and engineering of efficient mud systems.

Drilling fluids and drill cuttings are one of several waste streams from exploration and development activities in the oil and gas exploration and production sector. The term *drilling fluid* generally applies to fluids used to help maintain well control and remove drill cuttings (particles from underground geological formations) from holes drilled in the earth. Drilling fluids are essential, but they can pose a costly disposal problem for offshore operators who must haul spent mud and cuttings to shore for land disposal if they do not meet EPA discharge limitations and permit requirements.

As a result of prohibitions on the discharge of conventional oil-based muds and cuttings and increasing restrictions on the discharge of mineral oil-based drilling fluids, several types of non-aqueous drilling fluids have been developed, referred to as synthetic based muds (SBM). These technologically-advanced muds are used in areas where the discharge of muds and cuttings from conventional oil-based muds are restricted and where water-based muds cannot be used effectively. They yield drilling performances and safety similar to, or better than, conventional muds but have the added benefit of better environmental performance. The common characteristic of these fluids is that they have no detectable level of priority pollutants, which are a high priority concern of the EPA.

Beginning in 1991, the industry has asked EPA to formally evaluate these fluids and their acceptability for discharge. In 1994, the Department of Energy helped the industry begin a dialogue on this issue. An industry working group, established under the auspices of the National Ocean Industries Association (NOIA), initiated contact with EPA and MMS to confirm the regulatory status of synthetic drilling muds. Over thirty operators and mud companies have participated.

Several meetings were held during 1994 and 1995 on issues of concern. During this time the DOE's Argonne National Laboratory, a participant in the industry-agency discussions, published a report titled "Potential Environmental Benefits for Regulatory Consideration of Synthetic Drilling Muds" describing the operational, environmental and economic features of oil-based, water-based and synthetic drilling fluids.

This report also discusses potential EPA regulatory barriers to the wider use of synthetic based muds. Over the past year discussions with EPA have focused on these issues, primarily developing a definition for synthetic, the inverse emulsion prohibition, priority pollutant data and toxicity data. EPA has prepared draft definitions of "drilling fluid" and "synthetic material" that, when finalized, could remedy the existing discharge prohibition on inverse emulsions. Action that would remove regulatory barriers to the use of synthetic drilling muds is expected in the fall of 1996.

Solution: By working together, EPA, MMS, DOE, mud suppliers and the industry can clarify the regulatory situation to remove barriers to the widespread use of new technologies that improve the industry's environmental performance. This sensible discussion of the regulatory issues should be continued and resolved as quickly as possible to allow the industry the flexibility needed to utilize synthetic based drilling muds where appropriate.

This proposal *passes* the *common sense* test because it improves industry flexibility and encourages the adoption of new, better approaches, it relies on the best possible data, and it reduces industry costs without reducing environmental benefits.

Conclusion

Regulations that pass the common sense test should be the rule, not the exception. The public deserves no less. The issue is not, and never has been, retreating from environmental progress. Instead, the industry is committed

to building on past successes and, to do that, wants to ensure that environmental regulation is managed in the best possible way. With the unique exploration and production industry, this means relying on the expertise of decades of regulation in the states wherever possible. Regulators should also rely on the years of experience of the operating personnel in the regulated industries. If we work together to achieve common sense solutions, society—which runs on the energy we produce—and the environment will benefit together.

References

Potential Impact of Environmental Regulations on the Oil and Gas Exploration and Production Industry, American Petroleum Institute, March 1995, publication 815-13714

IOGCC Environmental Guidelines for State Oil & Gas Regulatory Programs, Interstate Oil & Gas Compact Commission, May 1994

Oil and Gas Exploration and Production Waste Management: A 17-State Study, U.S. Department of Energy Office of Fossil Energy and Interstate Oil and Gas Compact Commission, June 1993

Oil, Gas and the Environment—A State Regulatory Success Story, Interstate Oil and Gas Compact Commission, 1992

EPA/IOCC Study of State Regulation of Oil and Gas Exploration and Production Waste, 1990

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Economic Valuation of Ground Water in Remediation Decisions -- Will Benefit-Cost Analyses Be Useful?

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ABSTRACT

Benefit-cost analyses (BCAs) have been used in decision making related to surface water projects since the 1930s. In recent years, BCA applications have been made in ground water management, including regulatory impact analyses for required corrective actions for contaminated ground water and the development of economic justifications for local ground water protection programs. Passage of the Superfund laws directed attention to ground water remediation needs at sites characterized by historically improper disposal practices for hazardous wastes. Corrective action requirements have also been developed in response to the Resource Conservation and Recovery Act (RCRA) of 1984 wherein both waste disposal sites and leaking underground storage tanks (USTs) were addressed. The petroleum industry has been affected by ground water remediation requirements at numerous on-site and off-site waste disposal areas, including some Superfund sites, RCRA waste disposal sites, and UST sites. When ground water remediation is required, a key objective is to reduce health risks and restore the ground water resource to precontamination conditions. Cost considerations are typically based on relative comparisons of alternative remediation strategies after discounting their initial and operation and maintenance costs. The economic benefits of such remediation decisions are typically not considered from a quantitative perspective. Accordingly, a methodology for BCA of ground water remediation is described herein along with advantages and limitations relative to economically justifying remediation decisions and to prioritizing multiple site needs in an overall program. To do so, the Total Economic Value (TEV) of ground water must be recognized; the components of TEV include both use and nonuse services. Valuation techniques for such services include avoided costs, contingent valuation, and benefits transfer, among others. BCAs can be useful as integrating tools for information on remediation decisions, even if all benefits and costs cannot be quantified. Such studies should be based on an interdisciplinary approach which recognizes both technical and economic uncertainties associated with the results.

INTRODUCTION

Large expenditures have been made on ground water remediation efforts over the last 15 years. Such expenditures (costs) have been significant from national, industry, and individual company perspectives. Remediation efforts have often been required without due consideration of the environmental benefits resulting therefrom. Stated differently, the typical assumption is that the economic value of the ground water being cleaned up is at least equal to the remediation costs. Accordingly, the subject examined herein relates to the use of an economics-based tool; namely, benefit-cost analysis (BCA), in ground water remediation decision making. This tool should be considered as complementary to other currently used tools such as cost-effectiveness analysis (CEA), risk assessment (RA), and/or environmental impact assessment (EIA). Key sections within this paper are related to the total economic value (TEV) of ground water and identifying and quantifying remediation benefits. Summary observations are included on some generic advantages and disadvantages of BCA and on applications to ground water remediation.

HISTORICAL USAGE OF BCA

Benefit-cost analyses have been used in decision making related to developing multipurpose surface water reservoirs or flood control projects since the Flood Control Act of 1936 (1). Agencies involved in BCAs for water projects have included the U.S. Army Corps of Engineers, the U.S. Bureau of Reclamation, and several others. Two examples of recognized BCA techniques which are typically used to compare the economic feasibility of alternative plans are the Present Worth Method and the Benefit-Cost Method. Briefly, the essentials of both techniques are:

(1) The Present-worth Method determines the summation of the net present value (NPV) of all time (t) discounted benefits (B) minus all time (t) discounted costs (C) over the period of analysis (n). The NPV is a function of the interest rate (or discount rate r) used, and the NPV must be greater than zero (not negative) for a project to be considered as economically feasible. The calculation is as follows:

$$NPV = \sum_{t=o}^{t=n} \frac{B_t - C_t}{(1 + r)^t}$$

(2) The Benefit-cost Method determines the ratio (B/C) of the average annual values of all time discounted benefits and costs over the period of analysis. The average annual values are a function of the interest rate used, and the ratio must be 1.0 or greater for a project to be considered economically feasible. The calculation is as follows:

$$B/C = \frac{\sum_{t=o}^{t=n} \frac{B_t}{(1 + r)^t}}{\sum_{t=o}^{t=n} \frac{C_t}{(1 + r)^t}}$$

Within the last two decades BCA has been used for other types of environmental resource developments or management decisions; examples include timber harvesting, creation of ecological conservation areas, protection of wetlands, and surface water quality management planning.

BCAs have also been proposed or used for ground water development, protection, and/or remediation projects.

Currently, BCAs are required as part of the regulatory impact assessment (RIA) process conducted by the U.S. Environmental Protection Agency on major proposed regulations with an estimated cost in excess of $100 million (2). In relation to ground water remediation, the final rule making on corrective action for solid waste management units delineated cost estimates and the following three-step process for determining the potential benefits of corrective action requirements (3): identify the environmental resources that suffer physical, chemical, or biological degradation due to releases from hazardous waste facilities subject to corrective action (releases most often affect ground water and soils, and the areal extent of contamination is often greatest for ground water); identify the types of benefits (e.g., protection of ground water services) associated with preventing or alleviating contamination of these resources through corrective action; and estimate the value of the benefits.

In a guide for conducting CEAs and BCAs of state and local ground water protection programs, the U.S. Environmental Protection Agency (4) suggested that benefits can be considered as commodity or resource benefits; with the former including drinking water (individual use), agricultural uses, and industrial applications. Ground water can also be viewed as a commodity based on its interaction with surface waters and potential ecological services; this commodity value should be based on the value of the surface water ecosystem. Resource benefits include being able to use the ground water at some time in the future (option value), having a source of clean water for future generations (bequest value), and knowing that the ground water is uncontaminated, even if there is no expectation that it will ever be used (existence value). These concepts are basic to the total economic value (TEV) of ground water discussed later.

In terms of ground water protection, because it may not always be practical or even possible to measure commodity and/or benefits directly, a BCA approach would involve estimating the protection program's costs and then estimating the losses in well-being that are avoided by implementing a program that improves or maintains ground water quality. This approach allows estimation of the benefits that derive from the "avoided costs" of damages resulting from contamination, new or additional treatment, and/or development of alternative ground water supplies (4). A BCA study related to implementing wellhead protection programs in six smaller communities was recently completed (5 and 6). The "avoided cost benefits" were compared to the costs of a wellhead protection program for each community, with the resultant information aggregated into a B/C ratio. The average B/C ratio was 7:1.

OPPORTUNITIES FOR INCORPORATING BCA INTO GROUND WATER REMEDIATION DECISION MAKING

Passage of the 1980 Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund) and the 1986 Superfund Amendments and Reauthorization Act (SARA) directed attention to ground water remediation needs at sites characterized by historically improper disposal practices for hazardous wastes. Corrective action requirements have also been developed in response to the Resource Conservation and Recovery Act (RCRA) of 1984 wherein both waste disposal sites and leaking underground storage tanks (USTs) were addressed. These laws relate to the petroleum industry because it has been affected by ground water remediation requirements at numerous on-site and off-site disposal areas, including some Superfund sites, RCRA waste disposal sites, and other designated locations identified via the UST program.

The final decision on a remedial action plan for a Superfund site is typically based on relative cost comparisons of the alternatives, with the

presumption being that each viable alternative would achieve designated applicable or relevant and appropriate regulations (ARARs). Cleanup standards for non-Superfund sites can also be designated. This approach represents a type of CEA wherein the measure of effectiveness is not expressed in monetary terms; rather, expressions such as "reductions in relative risk," "number of lives saved," or "reductions in the population exposed" may be used. CEA can also be used for prioritization of remediation projects across several hazardous waste sites. For example, the performance criteria in one CEA methodology allow the ranking of remediation projects based on the lives saved per dollar of project expenditures (7).

From an economic perspective in remediation decision making based on CEA, the value of clean ground water can be considered to be equal or greater than the costs incurred by users to respond to ground water contamination. The money spent either to replace contaminated ground water or to treat ground water to lower the concentration of contaminants to an acceptable level thus represents the value (or benefits) of cleanup. In effect, this approach assumes a $B/C \geq 1.0$, and it is typically used in current remediation decisions associated with Superfund, RCRA, or UST sites. More comprehensive BCAs are typically not included as a basis for a fundamental go/no-go decision on clean-up, nor as an additional comparator for alternatives under consideration; however, their inclusion could enhance the information available to decision makers.

TOTAL ECONOMIC VALUE

An important concept related to the benefits of ground water remediation is the total economic value (TEV) of ground water. Basically, TEV can be defined as:

$$TEV = UV + NUV$$

where

UV = use values

NUV = nonuse values

Use values (UV) arise from the actual use made of the ground water; use values can be divided into direct use values (DUV), indirect use values (IUV), and option values (OV). DUV refers to actual uses such as for municipal (DUV_m), industrial (DUV_i), or agricultural (DUV_a) water supplies. IUV includes related functions and values of the ground water system, including the provision of stream baseflow (IUV_b) and the value associated with interrelationships with wetland systems (IUV_w). OV refers to the value approximating an individual's willingness-to-pay to safeguard the ground water now and preserve the option of using it at a future date.

Non-use values (NUV) typically include in-situ values (IV), a "passive use" or existence value (EV), and a bequest value (BV). IV basically encompasses the value of ground water as a buffer stock against the influence of droughts in surface water supplies (IV_b), the value of in-place ground water as a deterrent to longer-term land subsidence (IV_s) in areas characterized by previous overpumping of the resource, and the "inherent assimilative capacity" (or intrinsic bioremediation) value in terms of naturally occurring purification processes (IV_p). EV is unrelated to current use or OV, it simply occurs due to the existence of the ground water itself. BV relates to the value accruing to an individual from the knowledge that descendants or other future generations might benefit from the ground water resource.

In summary, the TEV of ground water can be rewritten as:

$$TEV = DUV_m + DUV_i + DUV_a + IUV_b + IUV_w + OV + IV_b + IV_s + IV_p + EV + BV$$

Relative to TEV applied in ground water remediation decision making, it should be recognized that the actual TEV depends on whether an"ex ante" (before contamination), "ex post" (after contamination), or "ex post with remediation" perspective is used (8). Comprehensive BCAs should include all three perspectives. TEV determination under any of these perspectives will require the cooperative efforts of hydrogeologists, biophysical scientists, engineers, and economists.

While TEV is useful in identifying the "true value" of ground water, it should be recognized that there is no agreement on the above classifications of the components. For example, another classification could be based on extractive services ($DUV_m + DUV_i + DUV_a$), ecological services ($IUV_b + IUV_w$), and in situ services ($OV + IV_b + IV_s + IV_p + EV + BV$). Further, valuation techniques for the components may overlap, and there are uncertainties regarding their results. Also, the available techniques may not be able to distinguish between all identified components in the process of attempting the quantification of each. Finally, not all of the above-listed values are equal; that is, some values may be considerably higher than others and thus can be ignored in certain situations.

METHODOLOGIES FOR BCA of REMEDIATION ACTIVITIES

Two methodologies related to BCA and ground water remediation will be briefly mentioned. Both methodologies could be applied to Superfund sites, RCRA waste sites, or UST sites. In the first example, the U.S. Environmental Protection Agency (3) developed a methodology for estimating the costs and benefits of site cleanup at hazardous waste treatment, storage, and disposal facilities regulated under RCRA. This methodology was developed to facilitate the compilation of national estimates; however, it could be used for site-specific analyses. Cost estimates are based on the capital, operation and maintenance, and investigatory components of each remedial activity. The total costs were adjusted to include design, oversight, and contingency assumptions, and then discounted using a mandated seven percent discount rate to account for the timing of remediations. Benefits measures included human health risk reduction, averted water use costs, and nonuse considerations. In addition, ecological risk under baseline conditions were estimated along with the effects of cleanup facilities on residential property values. Detailed information on the methodology is available elsewhere (3).

A seven-step methodology for integrating the typical components of a site remedial investigation/feasibility study, RA, and/or EIA, and BCA has been proposed (9). The seven steps are summarized in Table 1; additional details are available elsewhere (9). Step 5 represents the heart of the methodology relative to delineating remediation benefits; detailed components of Step 5 include:

(1) Qualitatively identifying the potential benefits of each alternative in relation to the ground water services affected by the contamination.

(2) Economically quantifying the benefits of each alternative for each ground water service through the use of engineering and hydrogeological information and other techniques as appropriate. Examples of techniques which could be used include for benefits related to avoided costs in relation to extractive services -- engineering feasibility studies and ground water usage studies; for benefits related to reductions in health risks -- risk assessment information and generic information on the value of a statistical life (cancer risk)

or the health costs of noncancer illnesses; for ecological benefits related to wetlands -- wetland habitat evaluation methods and generic information on the economic valuation of wetland habitat units; for ecological benefits related to the provision of base flows in rivers -- aquatic habitat evaluation methods coupled with an in-stream flow incremental methodology, and generic information on the economic valuation of stream habitat units; and for nonuse benefits -- carefully planned contingent valuation surveys (or possibly hedonic pricing techniques or benefits transfers).

(3) Determining the present value of the benefits over the remediation project life cycle.

Benefits Information

Table 2 summarizes some identified benefits associated with ground water remediation, and several conventional valuation techniques which can be used in their quantification (after 10). Table 3 provides a summary of several studies focused on either a specific valuation technique or the determination of specific use or nonuse values of ground water.

The valuation techniques in Tables 2 and 3 each have advantages and limitations (or uncertainties). Detailed information on these features is available in most water resources and/or environmental economics books. However, even though generic information is available, it has noted that there is limited evidence on using such techniques to value ground water resources (8). Of importance herein is to recognize the absence of any all-encompassing technique whose results would be accepted without question by all users. Accordingly, the issue of selecting one or more techniques for usage in a BCA study becomes important.

One widely used technique for measuring nonmarket values, which is typically the case for ground water services or values, is through directly questioning individuals regarding their willingness-to-pay for a service. This technique, which is called contingent valuation (CV), is typically based on a questionnaire survey. The dollar values obtained for the service are said to be contingent upon the nature of the constructed (hypothetical or simulated) market and the service described in the survey scenario. CV studies can also be conducted as face-to-face interviews or as telephone interviews (23 and 24). Even though CV is rather straightforward in its approach, the technique itself and the results have often been subject to questioning and controversy. Accordingly, a recent "blue ribbon" panel on CV sponsored by the National Oceanic and Atmospheric Administration has developed some minimum and recommended guidelines for conducting CV studies (25).

Benefits transfer (BT) is a valuation technique which is not listed in Table 2; however, it does have potential applicability. Briefly, BT refers to using benefits (values) estimates derived from one to several locations to value ground water quality and changes at another location. Stated differently, the transferability of benefits refers to the extent to which the process, demand function, and values estimated for one site can be applied to estimate the benefits attributable to another site elsewhere (26). To provide an example, if it were necessary to assess the benefits of remediating ground water pollution in a particular setting, a site specific study (using avoided costs and/or CV) could be commissioned. Expenditures for such a study would be incurred, and time would be required for study conduction. As an alternative, if a valuation study had been conducted at another remediation site with similar characteristics (demographics, scale, and extent of environmental problems), the benefits estimates from the original remediation site could be transferred to obtain benefits measures at the new site (22). Such "transfers" should be made with caution because of the inherent site specific nature of ground water contamination, ground water services and

the effects of contamination, and technically appropriate remediation technologies.

For some indirect use values such as those related to stream baseflow and wetlands, nonmonetary methods may be the only option for valuation. This would be analogous to the use of relative risk assessments in relation to human health risks from contaminated ground water. To illustrate some potentially useable nonmonetary methods, reference can be made to the Institute for Water Resources (IWR) of the U.S. Army Corps of Engineers; IWR is conducting research on both monetary valuation and nonmonetary evaluation of "environmental investment" decisions involving mitigation and/or restoration activities for surface water projects (27). Nonmonetary evaluation techniques are generally focused on various forms of habitat assessment to serve as a basis for measuring, in ecological terms, the impacts (benefits) of environmental improvement projects.

Remediation Cost Information

Due to the importance of cost considerations in decision making related to remedial action plans, it is critical that economically defensible estimates for both capital and operation and maintenance costs be developed. Due to the longer-term nature of many remedial action plans, it is also critical that technically defensible estimates of the time requirements for cleanup operations be developed. The latter estimates can be improved via the use of modeling. Site specific cost estimates are dependent on the uniqueness of site problems, the size or scale of the contaminated area, the collective history of the use of particular remediation technologies, and regional and local economic conditions. Due to potentially extensive time periods between initial site studies and the initiation of cleanup actions, inflation can become an important factor to consider both in terms of capital costs and operation and maintenance costs. Also, one of the problems in dealing with remedial action plan costs is the wide variations between initial cost estimates and the received contractor bids for the remediation work.

Even with these caveats regarding remediation costs, numerous reference materials regarding unit cost information have been produced. Such information can be useful in the development of both preliminary and final cost estimates for remediation plans. Two examples of cost information and methodological approaches will be briefly noted.

The Superfund CASHOUT computer model has been developed to enable calculation of the present value of cleanup costs at Superfund sites (28). This model can be used to develop settlement figures for potentially responsible parties (PRPs) for de minimus settlements; these settlements are commonly referred to as "cashouts." De minimus PRPs are parties whose contribution either to the amount or toxicity of hazardous substances, are minimal in comparison to other hazardous substances at the site, or who are considered innocent landowners of the site. By "cashing out" of the legal suit, the de minimus PRPs avoid prolonged legal expenses associated with hazardous waste liability suits.

A guidebook for the development of cost information on hazardous waste site remediation projects has been developed by a "roundtable" group of federal agencies consisting of members from the U.S. Environmental Protection Agency, the U.S. Department of Defense, the U.S. Department of Energy, and the U.S. Department of the Interior (29). Five levels of detail for the types of cost elements were suggested, with project cost documentation following an agreed-to interagency work breakdown structure (WBS) to the extent possible. The third level identifies 68 specific types of treatment processes. It is expected that the WBS format will be used in the future as part of federal procurements for site remediation services. Data collected through use of the WBS will be stored

electronically in an Historical Cost Analysis System (HCAS). This data could be used over time to refine remediation cost estimates.

EVALUATION OF BCA

Two perspectives can be identified regarding ground water valuation and its inclusion in BCA. First, such valuation elevates the benefits (or services) to an equal importance with typically utilized costs. Conversely, some have suggested that valuation reduces the resource value to routine comparisons to costs (30). For either perspective, it should be noted that the major strength of BCA is not necessarily the predicted outcome, which depends upon assumptions and utilized techniques, but the process itself, which forces an approach to decision-making that is based on systematic and quantitative reasoning. However, a major shortfall of BCA has been the difficulty of quantifying both benefits and costs of actions that effect environmental assets not normally bought and sold in markets (23); with this being particularly of concern for ground water remediation efforts. This section first addresses some generic advantages and limitations of BCA when applied in ground water remediation decision making. Some observations from two specific studies are then noted.

Some general advantages of BCA as a tool in decision making related to ground water remediation include:

(1) It is based on an established theory of value that has been scrutinized and debated by many economists and adjusted to meet some of its theoretical and operational shortcomings (31).

(2) It can aid in the identification of the "true costs" of using scarce ground water or of contaminating such resources. In this regard, BCA can be a reminder that ground water is not 'free,' even though there may not be a conventional market for all of its services (32).

(3) It attempts to reflect the values of all people rather than a select few, insofar as these values are revealed by the behavior of people in the marketplace or via the use preference surveys such as the contingent valuation method (31).

(4) In the context of BCA, valuing as many effects as possible narrows the field remaining for 'pure' judgments between noncomparable factors (32).

Some general disadvantages or limitations of BCA in relation to ground water remediation include:

(1) The willingness-to-pay criterion for placing values on ground water services violates the democratic principle of equality, because willingness-to-pay is greatly affected by the ability to pay (31).

(2) In its attempt to monetize all benefits and costs, BCA typically involves adopting a set of very technical procedures that are difficult for decision makers and the public to understand (31).

(3) There is serious doubt that dollar values can or should be placed on many types of environmental, social, and political impacts. These impacts relate to issues and problems that people do not equate with money. Even if monetary values were secured, say by personal interviews, their usefulness may be questioned (31). In fact, some individuals find the

monetarization of environmental aspects unacceptable on moral grounds (33).

(4) The cost of conducting a BCA can be very high. One of the prime reasons is that extensive research is necessary to derive monetary values for benefits that do not have immediate dollar equivalents (31 and 33).

(5) The procedure for discounting future costs and benefits creates serious intergenerational equity problems, potentially placing virtually no importance on long-term environmental damages and resource depletion (31). Further, the choice of a discount rate can have a considerable influence on a BCA; typically the B/C ratio decreases as the interest rate increases. Higher discount rates would give greater credence to the overexploitation of ground water resources, thus reflecting concerns related to intergenerational equity. Because of this and the perspective held by some that environmental resources should not be subjected to "traditional BCA" considerations, suggestions have been made that low to zero discount rates be used for remediation projects, or that distributional weights be assigned to the costs and benefits accruing to future generations (34).

(6) One of the problems associated with applying BCA to environmental management is that the ecosystems (or resources) addressed are complex in functions and interrelationships (30). Such complexity is certainly true relative to hydrogeological features of ground water systems, their interrelationships with surface water flows and wetland systems, and subsurface transport and fate processes.

(7) Benefits are typically considered from an "anthropocentric perspective"; that is, the worth of the ground water resource is only considered in terms of what it provides to human beings.

Following a late 1980s study focused on the use of BCA in Superfund remediation efforts, the following conclusions were developed (10):

(1) Even if benefits and costs can only be assessed and compared in a qualitative fashion, such a comparison should be a part of every remedial action decision.

(2) More quantitative benefit-cost analysis -- in which efforts are made to assign dollar values to many of the favorable and unfavorable effects -- should be undertaken for higher priority cleanup sites.

(3) It is important to note that a careful and defensible BCA could be quite expensive, particularly where complex ground water modeling and risk assessments are required. Although no "rules-of-thumb" or budget algorithms exist for BCA studies, they could easily reach six figures for a site.

(4) BCA is more useful if conducted prior to a remediation effort rather than after the fact, although there is also value in ex post analyses. For example, it would be useful to know whether cleanups that have already taken place have produced benefits in excess of costs.

One actual case applied BCA in a limited manner to a Superfund site in Woburn, Massachusetts (35). Benefits were determined via an "avoided cost" approach accounting for health costs and costs for an alternative

water supply. Numerous uncertainties were identified, particularly regarding ground water modeling, the effectiveness of contaminant source control and treatment measures, anticipated health effects, and perceived risks which could influence ground water usage as a municipal water supply. These uncertainties had obvious implications in quantifying resultant benefits and costs, and the NPV and B/C ratio for considered remediation alternatives.

SUMMARY AND CONCLUSIONS

The concept and applications of BCA in ground water remediation decision making have been presented herein. If BCA is to be useful in this context, additional theoretical development and practical applications will be needed. The following represent some conclusions related to using BCA in this manner:

(1) BCA is a potentially effective tool for integrating information related to remediating contaminated ground water at designated sites. The common metric for the information is the dollar. However, neither CEA nor BCA were ever intended by economists to be the only basis used in government policy decision making (10). Therefore, CBA must be recognized as only one tool which might be useful in remediation decision making. Other tools such as CEA, RA, and EIA may also be useful.

(2) One of the reasons for minimal economic information on ground water is that market-based pricing is typically not incorporated in ground water decisions (Moncur and Pollock, 1988). Therefore, the comprehensive estimation of ground water quality benefits requires more complete data than are currently available for remediation studies. Linkages must be made between measures of ground water quality benefits and man's activities in relation to improvements in ground water quality resulting from remediation efforts (22).

(3) In view of available information and methods on ground water values (benefits), a reasonable approach for incorporating BCA concepts into remediation decisions would be to categorize benefits into those which can be quantified and monetized, quantified but not monetized, or identified (descriptively addressed) only. Ground water professionals with various substantive area experience are needed to effectively plan and conduct remediation-focused BCAs. Further, recognition of the services provided by ground water, even if they are not all quantified, can be helpful in ground water management in general (36).

(4) There are numerous uncertainties which should be recognized in applying BCAs to ground water remediation. Such uncertainties may be related to (a) future demands and price structures for ground water usage; (b) the nature and extent of the ground water contamination problem; (c) the technical capabilities and effectiveness of considered remediation technologies; (d) the accuracy of ground water modeling results for different remediation scenarios; (e) the identification and valuation of local use and nonuse values of the ground water system; and (f) appropriate bases for selection of a discount rate to use in specific BCA calculations.

(5) A standardized protocol is needed for planning and conducting benefit-cost analyses of ground water remediation efforts. Such a protocol would need to be both articulated and field tested prior to its widespread usage.

(6) BCA of ground water remediation alternatives at contaminated sites can be used to justify or rule-out remediation efforts if the NPV is less than zero, or if the B/C ratio is less than one. However, this information needs to be coupled with specific regulatory requirements, information on actual and perceived risks, and CEA results in such "go-no go" decisions. NPVs and B/C ratios can also be used in selecting a remediation alternative (plan) for a contaminated site. In addition, these BCA measures could be used to prioritize remediation efforts across several sites, assuming that such measures have been developed for each site under consideration.

SELECTED REFERENCES

1. Galloway, G.E., "The Role of Social Sciences in Putting 'People' into Federal Water Resources Project Planning and Evaluation," in The Role of Social and Behavioral Sciences in Water Resources Planning and Management, Baumann, D.D. and Haimes, Y.Y., editors, American Society of Civil Engineers, New York, New York, 1988, pp. 313-326.

2. Harrington, W., "The Use of Benefit-Cost Analysis in Decision-Making: Three Examples from the EPA," EPA Cooperative Agreement CR-821821-01, August, 1995, Resources for the Future, Washington, D.C., pp. 1-3, and 14-21.

3. U.S. Environmental Protection Agency, "Regulatory Impact Analysis for the Final Rulemaking on Corrective Action for Solid Waste Management Units -- Proposed Methodology for Analysis," Draft Copy, March, 1993a, Office of Solid Waste, Washington, D.C., pp. 6-1 to 6-12.

4. U.S. Environmental Protection Agency, "A Guide for Cost-Effectiveness and Cost-Benefit Analysis of State and Local Ground Water Protection Programs," EPA 813-R-93-001, April, 1993b, Washington, D.C., pp. 25-28, 41-42, 57, and 65-86.

5. U.S. Environmental Protection Agency, "Benefits and Costs of Prevention: Case Studies of Community Wellhead Protection -- Volume 1," EPA 813-B-95-005, March, 1996a, Washington, D.C., pp. ES-1 to ES-5.

6. U.S. Environmental Protection Agency, "Benefits and Costs of Prevention: Case Studies of Community Wellhead Protection -- Volume 2 -- Detailed Case Studies of Seven Communities," EPA 813-B-95-006, March, 1996b, Washington, D.C.

7. Thompson, R.E., "Development of a Cost-Effectiveness Methodology to Prioritize Environmental Mitigation Projects," AFIT/GEE/ENP/93 S-02, September, 1993, Air Force Institute of Technology, Wright-Patterson AFB, Ohio.

8. Smith, V.K., "Valuing Ground Water Resources: A Conceptual Overview," Proceedings of Conference on Clean Water and the American Economy -- Vol. 2, Ground Water (October 19-21, 1992), EPA 800-R-93-001b, March, 1993, Office of Water, U.S. Environmental Protection Agency, Washington, D.C., pp. GW 1-5 to GW 1-13.

9. Canter, L.W., "Environmental Assessment and Economic Valuation of Ground Water Remediation Projects," Ch. in Integration of Environmental Assessment and Economic Valuation in Project Appraisal, Kirkpatrick, C., and Lee, N., Editors, Edward Elgar Publishing Company, London, England, 1996, in press.

10. Paulson, G., Portney, P.R., and Krupnick, A.J., "The Benefits and Costs of Superfund Cleanups: An Information Assessment," September, 1989, Center for Hazardous Waste Management, Illinois Institute of Technology, Chicago, Illinois, (report submitted to Coalition on Superfund, Washington, D.C.).

11. Edwards, S.F., "Option Prices for Groundwater Protection," Journal of Environmental Economics and Management, Vol. 15, 1988, pp. 475-487.

12. Abdalla, C.W., "Measuring Economic Losses from Ground Water Contamination: An Investigation of Household Avoidance Costs," Water Resources Bulletin, Vol. 26, No. 3, June, 1990, pp. 451-463.

13. Tsur, Y., and Graham-Tomasi, T., "The Buffer Value of Groundwater with Stochastic Surface Water Supplies," Journal of Environmental Economics and Management, Vol. 21, 1991, pp. 201-224.

14. McClelland, G.H., Schulze, W.D., Lazo, J.K., Waldman, D.M., Doyle, J.K., Elliott, S.R., and Irwin, J.R., "Methods for Measuring Non-Use Values: A Contingent Valuation Study of Groundwater Cleanup," October, 1992, University of Colorado, Boulder, Colorado.

15. Poe, G.L., and Bishop, R.C., "Measuring the Benefits of Groundwater Protection from Agricultural Contamination: Results from a Two-Stage Contingent Valuation Study," Staff Paper No. 341, May, 1992, Department of Agricultural Economics, University of Wisconsin-Madison, Madison, Wisconsin.

16. Sun, H., Bergstrom, J.C., and Dorfman, J.H., "Estimating the Benefits of Groundwater Contamination Control," Southern Journal of Agricultural Economics, Vol. 24, No. 2, December, 1992, pp. 63-71.

17. Abdalla, C.W., "Avoidance Costs and Ground Water Values: Results of Two Empirical Applications," Proceedings of Conference on Clean Water and the American Economy -- Vol. 2, Ground Water (October 19-21, 1992), EPA 800-R-93-001b, March, 1993, Office of Water, U.S. Environmental Protection Agency, Washington, D.C., pp. GW 2-17 to GW 2-23.

18. Crutchfield, S.R., "Issues in Measurement of the Non-Use Value of Ground Water," Proceedings of Conference on Clean Water and the American Economy -- Vol. 2, Ground Water (October 19-21, 1992), EPA 800-R-93-001b, March, 1993, Office of Water, U.S. Environmental Protection Agency, Washington, D.C., pp. GW 4-17 to GW 4-27.

19. Hauser, A., "Benefits of Improving Water Quality in the Abbotsford Aquifer: An Application of Contingent Valuation Methods," 1993, Environment Canada, Ottawa, Ontario, Canada.

20. Holland, M.M., "Issues and Research Needs in Valuing Ground Water: An Ecosystem Perspective," Proceedings of Conference on Clean Water and the American Economy -- Vol. 2, Ground Water (October 19-21, 1992), EPA 800-R-93-001b, March, 1993, Office of Water, U.S. Environmental Protection Agency, Washington, D.C., pp. GW 4-2 to GW 4-5.

21. Michaels, R.G., "When the Home is No Longer a Castle: Inferring the Economic Value of Ground Water Contamination from Residential Property Sales," Proceedings of Conference on Clean Water and the American Economy -- Vol. 2, Ground Water (October 19-21, 1992), EPA 800-R-93-001b, March, 1993, Office of Water, U.S. Environmental Protection Agency, Washington, D.C., pp. GW 2-34 to GW 2-41.

22. Crutchfield, S.R., Feather, P.M., and Hellerstein, D.R., "The Benefits of Protecting Rural Water Quality: An Empirical Analysis,"

Agricultural Economic Report No. 701, January, 1995, Economic Research Service, U.S. Department of Agriculture, Washington, D.C.

23. Lipton, D.W., Wellman, K., Sheifer, I.C., and Weiher, R.F., "Economic Valuation of Natural Resources -- A Handbook for Coastal Resource Policymakers," Decision Analysis Series No. 5, June, 1995, National Oceanic and Atmospheric Administration, NOAA Coastal Ocean Office, Silver Spring, Maryland, pp. 1, 29-31, 42, 50-54, and 63-64.

24. Field,, B.C., Environmental Economics: An Introduction, McGraw-Hill Book Co., Inc., New York, New York, 1994, pp. 139, 149 and 150.

25. Arrow, K., Solow, R., Leamer, E., Portney, P., Randner, R., and Schuman, H., "Report of the NOAA Panel on Contingent Valuation," Federal Register, Vol. 58, No. 10, January 15, 1993, pp. 4602-4614.

26. Willis, K.G., and Garrod, G., "Transferability of Benefit Estimates," Ch. 12 in Environmental Valuation -- New Perspectives, Willis, K.G., and Corkindale, J.T., editors, CAB International, Wallingford, England, 1995, pp. 191-212.

27. Feather, T.D., Russell, C.S., Harrington, K.W., and Capan, D.T., "Review of Monetary and Nonmonetary Valuation of Environmental Investments," IWR Report 95-R-2, February, 1995, Institute for Water Resources, U.S. Army Corps of Engineers, Alexandria, Virginia, pp. 3-6, 36-46, and 100.

28. Industrial Economics, Inc., "Superfund Cashout User's Manual," PB 94-141678, September, 1992, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia.

29. Federal Remediation Technologies Roundtable, "Guide to Documenting Cost and Performance for Remediation Projects," EPA-542-B-95-002, March, 1995, U.S. Environmental Protection Agency, Washington, D.C., pp. 1, 9-13, and 38-42.

30. Hanley, N., "The Role of Environmental Valuation in Cost-Benefit Analysis," Ch. 4 in Environmental Valuation -- New Perspectives, Willis, K.G., and Corkindale, J.T., editors, CAB International, Wallingford, England, 1995, pp. 39-55.

31. McAllister, D.M., Evaluation in Environmental Planning, Fourth Printing, MIT Press, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1988, pp. 140-143.

32. Winpenny, J.T., Values for the Environment -- A Guide to Economic Appraisal, Overseas Development Institute, HMSO, London, England, 1991, pp. 6-7, 42-72, and 76-80.

33. Barde, J.P., and Pearce, D.W., Valuing the Environment, Earthscan Publications, Ltd., London, England, 1991.

34. Organization for Economic Co-operation and Development, "The Economic Appraisal of Environmental Projects and Policies -- A Practical Guide," 1995, Paris, France, pp. 131-134.

35. Spofford, W.O., Krupnick, A.J., and Wood, E.F., "Uncertainties in Estimates of the Costs and Benefits of Groundwater Remediation: Results of a Cost-Benefit Analysis," Discussion Paper QE 89-15, April, 1989, Resources for the Future, Washington, D.C.

36. Boyle, K.J. and Bergstrom, J.C., "A Framework for Measuring the Economic Benefits of Ground Water," Rep. 459, August, 1994, Maine Agricultural Experiment Station, University of Maine, Orono, Maine.

Table 1

Suggested Steps for Incorporating BCA into Site Specific Decision Making Regarding Ground Water Remediation (after 9)

Step 1:	Characterize the Ground Water Resource(s) at the Designated Contaminated Site (focus should be on resource without the presence of contamination; that is, the background conditions).
Step 2:	Describe the Ground Water Contamination and/or Usage Problem(s) Which Caused the Site to be Included on the Superfund National Priority List (NPL) for Nongovernmental Sites, or a Prioritized List for Governmental Sites; or Included in any Specified Ground Water Cleanup Requirements.
Step 3:	Delineate Institutional Requirements, Constraints, and/or Policies (including cleanup standards for various ground water contaminants; secondary requirements which might limit the usage of any remediation technology; and direct ground water usage restrictions or those related to maintenance of base flows in rivers, or to wetlands maintenance and preservation).
Step 4:	Define Potential Remediation Alternatives and Summarize Discounted Costs and Effectiveness Information for Each.
Step 5:	Delineate Potential Benefits of Remediation Alternatives (see text for details on this step).
Step 6:	Develop and Summarize Economic Information (Costs and Benefits) on Each Remediation Alternative (for each alternative develop NPVs and B/C ratios; for costs or benefits which have been identified but not quantitatively included in the analysis develop a table which qualitatively displays the influence of each nonincluded item on NPVs and B/C ratios).
Step 7:	Display the Decision Factors Related to the Remediation Alternatives and Choose the Alternative to Become the Recommended Action (list the key decision factors; develop a decision matrix table wherein the decision factors are displayed versus the remediation alternatives; complete the table by including summary quantitative or qualitative (descriptive) information for each alternative relative to each decision factor; utilize systematic decision support systems to conduct a trade-off analysis; and based on the results, identify the alternative which will become the recommended action).

Table 2

Benefit Categories from Ground Water Remediation and Valuation Techniques (after 10)

Benefit Category	Valuation Techniques
TO INDIVIDUALS:	
Health	
Mortality	•Wage Compensation •Contingent Valuation •Averting Behavior •Human Capital (foregone earnings)
Morbidity	•Averting Behavior •Contingent Valuation •Cost of Illness
Anxiety	•Contingent Valuation
Aesthetics	•Contingent Valuation
Loss of Independence	•Contingent Valuation
TO PRODUCTION:	
Crops/Forests/Fisheries	•Consumer Plus Producer Surplus
Water-Using Industry	•Same
Municipal Water Supply Authorities	•Opportunity Cost (alternative aquifer) •Service Replacement (municipal treatment, bottled water)
TO ECONOMIC ASSETS:	
Materials (corrosion)	•Replacement Cost •Service Values
Property Values	•Hedonic Price Models
TO ENVIRONMENTAL ASSETS:	
Use	
Recreation	•Unit Day •Contingent Valuation •Property Value •Travel Cost
Other	•Service Replacement •Contingent Valuation •Property Valuation
Nonuse (existence)	•Contingent Valuation

Table 3

Chronological Listing of Examples Use of Valuation Techniques

Reference	Description of Study
Edwards (1988) (11)	Description of a contingent valuation study of option prices (or household's willingness to pay to keep the option of further uses of ground water) to prevent uncertain, future nitrate contamination of a potable supply of ground water in Cape Cod, Massachusetts.
Abdalla (1990) (12)	Central Pennsylvania case study related to measuring economic losses from ground water contamination through the usage of the averting expenditures (avoidance costs) method.
Tsur and Graham-Tomasi (1991) (13)	Determination of the buffer value of a stock of ground water when used in association with a stochastic source of surface water for agricultural irrigation purposes. Buffer value is defined as the difference between the maximal value of a stock of ground water under uncertainty and its maximal value under certainty where the supply of surface water is stabilized at its mean.
McClelland, et al. (1992) (14)	Description of a comprehensive contingent valuation study to determine the total benefits (including use, altruistic, bequest and existence values) of cleaning up contaminated ground water; the resultant information can be used nationally to evaluate a variety of programs including Superfund and RCRA. Further, the results could be used in a benefit transfer mode for specific sites. Altruistic value refers to the value that households place on other households having clean ground water today. The study also determined that several sociodemographic and regional variables were found to be significant in explaining willingness-to-pay, including income, age, and education.
Poe and Bishop (1992) (15)	Description of a two-stage contingent valuation study, conducted in Portage County, Wisconsin, of the benefits of ground water protection from agricultural nitrates.
Sun, Bergstrom, and Dorfman (1992) (16)	Description of a contingent valuation study to measure the benefits of ground water contamination control (via an option price or individual's maximum willingness-to-pay to secure the option of using the ground water resource in the future) in an agricultural area in southwestern Georgia.
Abdalla (1993) (17)	Two case studies on the use of avoidance costs (averting expenditures) for estimating certain ground water values.
Crutchfield (1993) (18)	Discussion of issues related to the measurement of non-use values of ground water.
Hauser (1993) (19)	Use of contingent valuation method to determine the benefits of management measures to reduce nitrate pollution from agricultural practices in the Abbotsford aquifer in British Columbia, Canada.
Holland (1993) (20)	Connectivity between river and ground water systems in relation to ecological benefits (services) of ground water.
Michaels (1993) (21)	Use of residential property sales (property value studies) as an indication of the economic value of ground water contamination; and the influence of public perception on such sales.
Crutchfield, Feather, and Hellerstein (1995) (22)	Benefits transfer study related to ground water valuation in four agricultural regions in the United States.