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Proceedings of the Third International Petroleum Environmental Conference

September 24 - 27, 1996

Albuquerque, NM

Volume I

Edited by
Kerry L. Sublette

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Remediation of Brine-impacted Soil and Modeling of Subsurface Transport

Electrokinetic Leaching of Brine-Impacted Soils

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Abstract:

Brine-impacted soil continues to be a significant environmental problem associated with petroleum and natural gas production. It is imperative that brine spills be remediated. The most common remediation method, leaching, is plagued by poor water utilization efficiency. This issue may be addressed by electrokinetic leaching (EKL), a process in which a potential is applied across electrodes placed in water-saturated soil. However, the results from laboratory experiments with the EKL process provide a mixed view of its feasibility. With sand as the test material, the total amount of chloride ion recovered is actually reduced by an applied potential. This behavior results primarily because the passage of Cl^- toward (through) the cathode is greatly inhibited by the repulsive electrostatic forces acting upon the anion. Similarly, the passage of sodium ion through the anode is diminished. However, in experiments with the clay material kaolin, sodium ion recovery was clearly enhanced when a potential was applied to the cell. This effect was attributed to hydrogen ion, produced at the anode, promoting the exchange of Na+ from the clay particles. Experiments with soil were again dominated by electrostatic interactions between the contaminant ions and the two electrodes. The effect of electrode reaction products on the hydraulic conductivity near the cathode was also found to be important.

INTRODUCTION

Salt water is typically produced along with petroleum. At one time it was common practice for the "produced water" to be discharged at the surface. At the Big Lake Field in Texas, for example, approximately 200 million barrels of brine were released during 30 years of oil production, resulting in approximately 11 square miles of "brine-impacted" soil (1). It is no longer accepted practice to dispose of produced water in this manner; instead, the brine is "reinjected" beneath the surface. However, it is still quite common for some brine to be spilled during handling at the surface. Thus, brine-impacted soil continues to be a common environmental problem associated with the petroleum and natural gas industries.

Soil that is contaminated with salt is referred to as "saline". High soil salinity will result in the death of established plants. Soil that is unable to support plant life will eventually experience erosion, resulting in the formation of a "salt scar" (1). Also, the salt that leaches from brine-impacted soil may eventually find its way to nearby surface waters or groundwaters (2). In regions where rainfall is not plentiful, this "secondary contamination" of water resources may be of even greater consequence than the contaminated soil itself.

Leaching with rainwater is the most common approach to the remediation of brine-impacted soil. In those areas where rainfall is not plentiful, the efficiency of leaching may be enhanced by constructing a series of dikes. For example, the Texon Scar reclamation project (1) utilizes approximately 30,000 meters of levees over 100 hectares of land. The dikes are approximately 0.50 m high, and are spaced 40 meters apart.

When a brine-impacted soil experiences periods of dryness, evaporation will draw the salty leachate back toward the surface (3). Leachate flow can be maintained in a single direction through an irrigation treatment known as "ponding": after surrounding the contaminated area with dikes, the irrigation water is added rapidly to a prescribed depth. Ponding has proven successful in the remediation of the drilling fluid reserve pits (4); the application of 1 meter of fresh water reduced the electrical conductivity (a measure of soil salinity) of the upper 45 cm of the soil by an average of 59%.

Oilfield brines typically contain high concentrations of sodium ion. Such brines will also convert soil to the "sodic" condition, in which most of the cations associated with the surfaces of clay minerals have been replaced by Na^+. Sodic

soils exhibit poor hydraulic conductivity (permeability to water) because Na^+ exchange causes the clay particles to disperse and plug off the small pores through which the water would otherwise flow. The use of "amendments", or additives, to overcome poor hydraulic conductivity is widespread. The most widely used amendment is gypsum, a mineral composed primarily of calcium sulfate. The calcium ion released by this material reduces the swelling and dispersion of clays. In a series of column leaching experiments designed to simulate a ponding treatment, De Jong (5) demonstrated that gypsum mixed throughout the soil was more effective at enhancing hydraulic conductivity and the efficiency of leaching than surface-applied surface. This behavior would appear to be related to the limited solubility of calcium sulfate. When calcium nitrate was used in place of calcium sulfate, surface application also provided efficient leaching.

In the further development of leaching (i.e. ponding) as a means of remediating brine-impacted soil, two potential problems should be addressed. First, since irrigation water may be scarce or relatively expensive in some regions, the efficiency of its utilization must be enhanced. Secondly, if the secondary contamination noted above is a concern, a leachate collection system must be installed. Both of these issues are addressed by the remediation process known as electrokinetic leaching (EKL). This process, which involves the application of a potential across electrodes placed in water-saturated soil, may allow for more efficient utilization of the leaching water. Collection of the leachate from the "wells" in which the electrodes are placed is an integral part of this process.

A number of studies, involving both laboratory experiments and field testing, have considered the use of electrokinetic leaching for remediating soils contaminated with heavy metals (e.g. 6,7). The results of preliminary experiments concerning the electrokinetic leaching of brine-impacted soils were presented at the previous International Petroleum Environmental Conference (8). This report concerns the further development of the EKL process. In these laboratory experiments, the effect of different soil characteristics, soil amendments and leachate flow regimes were examined.

EXPERIMENTAL METHODOLOGY

The cell in which the electrokinetic remediation experiments were conducted was constructed of Plexiglas. It was 25 X 7.5 X 5 cm, and was capable of accomodating up to 500 g of sand (or somewhat smaller amounts of less dense test materials). A "drain" for collecting the leachate was incorporated at either end of the cell. To prevent the test material from entering the drains, the openings were covered first by pieces of stainless steel screen (Goodfellow Co.), which also served as an electrode in those experiments in which a potential was applied, and then by strips of qualitative filter paper (Fisher Scientific). Also, a strip of parafilm was used to seal off that portion of the filter paper that extended above the top of the sample bed; this prevented water from passing through the filter paper without first passing through the soil.

The test cell was used in two different configurations in this study. In the incremental (I-B) and bi-directional configuration, distilled water was added to the cell in 50 mL increments, and leachate was allowed to pass freely out of the cell through both drains. Typically, leachate drainage was "complete" (i.e. drainage had ceased, and a total of 50 mL of leachate had been collected) in 10 minutes or less. It was found to be convenient to collect the leachate in graduated, 50-mL polyethylene centrifuge tubes. In the second configuration, referred to as continuous and uni-directional (C-U), one of the drains was connected to a reservoir from which distilled water flowed at a constant rate. Leachate was collected, in 50 or 100 mL increments, at the other drain. To prevent water from pooling on top of the test bed, the rate of water flow through the system was regulated with the ground glass stopcock on the reservoir and an adjustable clamp on the tube attached to the outlet drain.

Experiments were conducted with three types of sample material. The materials included silica sand and kaolin purchased from Aldrich Chemical Co., and a sample of soil collected in the Nature Conservancy's Tall Grass Prairie Preserve, in Osage County, Oklahoma. In each case the sample material was relatively free of soluble salt initially. Prior to an experiment, the sample material was contaminated with known amounts of NaCl. With the sand and the soil, the sample and salt were mixed dry, poured into the cell, and then distributed with a spatula. When the kaolin was handled in this manner, large portions of the test bed were not wetted by the water added to the cell. Thus, the kaolin-salt mixture was first mixed in a beaker with sufficient water to produce a thick paste, which was then transferred to the cell with the aid of a rubber spatula.

In those experiments where a potential was applied to the cell, a Model BPS-103 (Hampden) power supply was utilized. Both the potential and current were monitored with multimeters. The temperature of the test bed was also monitored, with a thermometer.

Each leachate sample was analyzed for chloride and sodium ion by direct potentiometry, using a Fisher Accumet Model 800 pH meter, a saturated calomel reference electrode and either a glass sodium-selective electrode or a solid state chloride-selective electrode. A series of dilute sodium chloride solutions, produced from ACS reagent grade NaCl (Fisher), was used to calibrate the electrodes.

When a potential was applied to the cell, the leachate collected from the drain adjacent to the anode was quite acidic. As a result of the mass balance on Na^+ that was performed in the experiments with sand, it was discovered that this excess of hydrogen ion produced a significant positive error in the potentiometric determination of the Na^+ concentration. Thus, these samples needed to be neutralized, specifically with a source of alkalinity free of monovalent cations. The addition of calcium hydroxide and calcium carbonate were both considered for this purpose. The latter was eventually chosen because 1) the continued presence of the solid indicated that an excess of alkalinity had been added and 2) the cessation of bubbling indicated that neutralization was complete. However, even when this adjustment was made, the amount of Na^+ recovered from the test material still exceeded the amount known to have been added in a few experiments.

Similarly, the determination of chloride ion was found to be influenced by the ferric and chromic ions that accumulated in the leachate of the anode drain. These species arise through corrosion of the stainless steel screen, which occurs readily in acidic chloride media. These metal ions are able to form soluble complexes with Cl^-, thus reducing the concentration of "free" Cl^- to which the indicating electrode responds. Since this interference appeared to be of minimal importance, no attempt was made to correct for it.

RESULTS AND DISCUSSION

Sand, B-I Configuration: This study began with experiments that utilized the cell in the incremental and bi-directional (B-I) configuration. These experiments involved 500 g of "reagent-grade" sand, contaminated with 5.0 g of

NaCl (1.0 % by weight). Potentials ranging from 25 to 75 volts were applied in the experiments. Control experiments, in which no potential was applied, were also conducted.

The cumulative volumes of leachate collected at the anode (referred to as Drain 1 when no potential was applied) are presented in Fig. 1a. It can be seen that as the applied potential is increased, the volume of leachate collected from this drain decreases. Not surprisingly, the opposite trend is observed in the data corresponding to the cathode drain (Fig. 1b). In these plots the 25 V data set has been omitted because they are indistinguishable from the 0 V data. Also, the 50 V data, being identical to the 75 V data, have been omitted from Fig. 1b.

The enhancement in the volume of leachate passing through the cathode is consistent with the phenomenon known as electroosmosis. The extent of electroosmosis increases as the total electrolyte concentration of the solution decreases. Since most of the salt is removed early in a leaching experiment, electroosmosis should become more evident as the experiment progresses. Indeed, it can be noted in the figures that the difference between the 75 V and the 0 V leachate values increases with increasing water input.

The total chloride ion data for the I-B experiments with sand are displayed in Fig. 2a. It can be seen that only in the case of no applied potential does the cumulative amount of Cl^- leached equal the amount added. The application of a potential actually diminishes the total amount of Cl^- leached. The magnitude of this reduction scales to some extent with the magnitude of the potential applied to the cell.

The cumulative chloride ion data corresponding to the individual drains are presented in Figs. 2b and 2c. In Fig. 2b it can be seen that in the 0 volts case, the cumulative amount of Cl^- collected at the anode exceeded one-half of the known amount added (indicated by the horizontal, dotted line in the plot) by a slight margin. The opposite behavior can be observed in Fig. 2c. These results are consistent with slight non-uniformity in the flow of water through this type of sample material. When a potential of 50 or 75 V was applied to the cell, the cumulative amount of Cl^- recovered through the Anode Drain exceeded that of the control experiment, particularly at the lower input volumes. In Fig. 2c it can be seen that the application of a potential reduces the cumulative amounts of Cl^- leached from the Cathode Drain well below the one-half value. The leachate in this case was basic.

Two possible explanations for this behavior can be formulated. The first is based on electrostatics. Since the hydrogen ions produced by the anodic half-reaction are positively charged, they would be expected to attract anions (e.g. Cl^-), and to repel cations (e.g. Na^+). The opposite behavior would be expected to occur at the cathode. The experimental results are mostly consistent with this hypothesis. The second explanation relates to the electroosmosis that occurs in this system. Since electroosmosis occurs more readily in water with low salinity, this phenomenon may selectively withdraw fluid from the test bed that is lower in salinity.

The total cumulative amount of sodium ion in the leachate from both drains is presented in Fig. 3a. It can be noted that the amount of sodium leached from the sand was highest with the two intermediate potentials. In both of these cases the total amount of sodium leached exceeded the amount added to the sand. It is likely that these two data sets are slightly in error as a result of the interference from H^+ experienced by the Na^+ electrode.

Plots of the cumulative amount of Na^+ leached through the the individual drains are presented in Figs. 3b and 3c. In the case of the anode drain, it can be seen that the data for the 75 V experiment are quite low. Since it is in the leachates from the anode that the analytical error in the Na^+ determination is expected, it would appear that the data for the 25 and 50 V cases should be lower, perhaps even lower than the data for the case of no potential applied. In any event, the 75 V data suggest that Na^+ experiences repulsion at the anode. In Fig. 3c it can be seen that the amount of Na^+ recovered at the cathode is much greater than the "one-half amount" when a potential is applied. In this case there is no interference from hydrogen ion in the analytical results for Na^+; the leachate fractions were basic. These results appear to be consistent with electrostatic repulsion between Na^+ and the cathode half-reaction products.

The results from these experiments provide a mixed view of electrokinetic leaching, at least for sand. Electroosmosis is indicated by enhanced flow from the cathode drain; however, this phenomenon becomes apparent only after most of the salt has been leached from the sand bed. The total amount of Cl^- recovered is actually reduced by an applied potential. This behavior results primarily because the passage of Cl^- through the Cathode Drain is greatly inhibited, presumably as the result of repulsive electrostatic forces acting upon the anion. Similarly, the passage of Na^+ is greatly diminished through the Anode Drain, and greatly enhanced through the Cathode Drain, with increasing potential.

Sand, C-U Configuration: Experiments were also conducted with sand and the cell in the continuous and uni-directional (C-U) configuration. The flow of water through the cell was somewhat faster in this case relative to the I-B configuration, even when the outlet drain was partially constricted. Experiments were conducted with an applied potential of 50 V, and having the leachate pass out of the cell through either the Anode Drain or the Cathode Drain. Neither configuration provided more efficient leaching of Cl^-, and while higher concentrations of Na^+ were measured in the leachate when it passed out the Anode Drain, it is likely that this result is in error as a result of the H^+ interference. Thus, there appears to be no advantage to applying a potential to this leaching configuration when the contaminated material is sand.

Kaolin; C-U Configuration: One series of experiments was conducted with kaolin. This material was chosen because it exhibits a much finer particle size than sand, yet does not undergo excessive cation exchange or swelling as do some other clays. Also, a number of the electrokinetic remediation studies conducted by others have utilized kaolin as the test material. Sodium chloride was also added to this material, at a concentration of 1.0 % by weight, before each experiment.

As expected, the hydraulic conductivity of the kaolin proved to be much lower than that of the sand. This particular kaolin exhibited sufficient swelling to limit leachate flow to insufficiently low values, particularly when the cell was operated in the continuous and uni-directional (C-U) mode. Some improvement in this regard was achieved when 0.5 % by weight of calcium nitrate was added to the material before placing it in the cell. Also, it was discovered that the clay could be loaded into the cell more consistently if it was first mixed with water in a beaker, and stirred vigorously to form a paste. This technique was employed in all of the tests discussed below.

The first set of data presented addresses the effect of having the leachate flow out through the anode or the cathode, and the effect of the applied potential in the latter case. An experiment in which a potential was not applied served as the control. As indicated by the 0 volt data presented in Fig. 4a, the efficiency of recovery (i.e. the amount of Cl^- and Na^+ recovered per unit volume of water) was found to be much lower with the kaolin than with the sand. However, much larger amounts of Na^+ were recovered when a potential was applied to the cell; in fact, the amount of Na^+ recovered exceeded the amount added to the kaolin (as NaCl). In the experiment where the leachate flowed out of the Anode Drain (Fig. 4b), the leachate samples were acidic and were thus treated with calcium

carbonate prior to analysis. Even with this adjustment, one might conclude that these results were affected by the analytical interference. However, an excessive amount of Na^+ was also recovered when the leachate flowed out of the cathode (Fig. 4c), and the leachate in this case was strongly basic.

The results above suggested that the as-received kaolin, unlike the sand, possessed a significant exchangeable sodium ion content. To test this hypothesis, a sample of the as-received kaolin (i.e. not intentionally contaminated with NaCl) was tested with an applied potential of 50 V. It can be seen in Fig. 5 that some Na^+ is recovered from the kaolin even in this case. This is consistent with the Na^+ being exchanged on the surface of the clay particles, rather than being present as free salt (NaCl or otherwise). This exchangeable Na^+ has no incentive to desorb from the clay if leaching is conducted solely with fresh water. However, the addition of calcium nitrate to the clay, and the application of a potential to the cell, would appear to facilitate Na^+ exchange.

Hydrogen ion produced at the anode when a potential is applied to the cell may be the cation that is promoting the exchange of sodium ion from the clay particles. If this is indeed true, then the configuration in which the leachate flows from the anode toward the cathode should take greatest advantage of this phenomenon. The H^+ produced at the anode will permeate throughout the entire test bed in this case.

Soil, I-B Configuration: Experiments were also conducted with one soil sample. This sample was neither saline nor sodic initially. An amount of NaCl corresponding to a concentration of 1.0 % by weight was mixed into the soil before placing it in the cell.

The first series of experiments involved the incremental and bi-directional (I-B) configuration. In two of the experiments 0.5 % by weight calcium nitrate was also mixed into the soil. In Figs. 6a and 6b it can be seen that this amendment had little effect on the uniformity of leachate flow from the cell. However, the application of 50 V to the cell produced a significant increase in the flow of leachate from the Anode Drain, and a corresponding decrease in the flow from the Cathode Drain. This behavior may be attributed to a change in the structure of the soil resulting from the significant increase in pH that occurs in the vicinity of the cathode. This effect is apparently so dominant that electroosmosis cannot be detected.

The effect of calcium nitrate and an applied potential of 50 V on the leaching of chloride is presented in Figs. 7a and 7b. The cumulative amount of Cl^- recovered from Drain 1 (the Anode Drain when a potential was applied) is presented in Fig. 7a. It can be seen that the Cl^- leaching efficiency is increased first by the calcium nitrate, and then also by the application of a 50 V potential. Also, by comparing the data in Figs. 7a and 7b it can be seen that the cumulative amounts of Cl^- recovered from the two drains is more similar in the presence of the Ca^{2+}. This behavior is consistent with the effect of Ca^{2+} on hydraulic conductivity. The effect of the applied potential on the recovery of Cl^- can be attributed to its electrostatic attraction to the H^+ produced at the anode. The corresponding data for Drain 2 (the Cathode Drain) are presented in Fig. 7b. Here, it can be seen that the application of a potential reduces the recovery of Cl^- to almost zero. This behavior is consistent with repulsion by the hydroxide ions produced at the cathode. The recovery of Cl^- through the cathode is further diminished by the reduced flow of leachate through this drain.

The recovery of Na^+ from the contaminated soil is presented in Figs. 8a and 8b. It can again be seen that the addition of Ca^{2+} to the soil made the flow of leachate out both drains more uniform. It can also be noted that the application of a potential does not enhance the recovery of Na^+ through the Drain 1 (the Anode Drain). In the case of Drain 2, the amount of Na^+ in the leachate was initially lower in the case of the applied potential. This is consistent with the reduced leachate flow rate through the Cathode Drain observed under these condition.

The results above suggest that the electrokinetic leaching of brine-impacted soil in the incremental and bi-directional configuration is dominated by electrostatic interactions between the contaminant ions and ions produced at the two electrodes. The effect of electrode reaction products on the hydraulic conductivity near the cathode is also important. In any event, the application of a potential does not appear to provide enhanced efficiency of leaching beyond that provided by the amendment, calcium nitrate.

Soil, C-U Configuration: The effect of having the water flow continuously through the cell (the C-U configuration) was examined in two experiments with the soil. Calcium nitrate, at a concentration of 0.5 %, was added to the soil in both tests. A potential of 50 V was applied in both cases. The only difference between the two tests was that the leachate flowed out Drain 1 (the Anode Drain) in one experiment, while it flowed out the other drain (the Cathode Drain) in the other. In Fig. 9a it can be seen that the recovery of Cl^- was greater when the flow was through the anode; this is consistent with the results

obtained with sand, which were attributed to electrostatic repulsion acting upon the Cl^-. A comparison of Figs. 9a and 9b shows that the direction of water flow through the cell had little effect on the recovery of Na^+, and that more Cl^- than Na^+ is recovered in these tests. This is opposite to the behavior observed with the kaolin, in which enhanced recovery of Na^+ was attributed to enhanced exchange of Na^+ from the clay by H^+ produced at the anode. An explanation for this discrepancy has not yet been formulated.

SUMMARY AND CONCLUSIONS

Brine-impacted soil continues to be a significant environmental problem associated with petroleum and natural gas production. It is imperative that brine spills be remediated; the salt limits the ability of plant life to control erosion, and when leached out, may contaminate nearby surface waters and groundwaters. The most common remediation method, leaching with water, has two potential drawbacks. First, since water may be scarce or relatively expensive in some regions, the efficiency of its utilization must be enhanced. Secondly, a leachate collection system may be needed to control salt migration. Both of these issues may be addressed by electrokinetic leaching (EKL), a process in which a potential is applied across electrodes placed in water-saturated soil. Collection of the leachate from the electrode "wells" is an integral part of the EKL process.

The results from laboratory experiments with the EKL process provide a mixed view of its feasibility. With sand as the test material, and the EKL test cell utilized in the incremental and bi-directional configuration, the total amount of chloride ion recovered is actually reduced by an applied potential. This behavior results primarily because the passage of Cl^- toward (through) the cathode is greatly inhibited, presumably as the result of repulsive electrostatic forces acting upon the anion. Similarly, the passage of sodium ion through the anode is diminished. While electrostatic attraction provides enhanced recovery at the oppositely charged electrodes, this effect does not fully compensate for the repulsion.

Experiments with the clay material kaolin, and the cell in the continuous and uni-directional configuration, provided more encouraging results. Sodium ion recovery was clearly enhanced when a potential was applied to the cell. This effect was attributed to hydrogen ion, produced at the anode, promoting the exchange of sodium ion from the clay particles.

Experiments with soil, and with the cell in the incremental and bi-directional configuration, were again dominated by electrostatic interactions between the contaminant ions and the two electrodes. The effect of electrode reaction products on the hydraulic conductivity near the cathode was also found to be important. In any event, the application of a potential did not appear to provide enhanced efficiency of leaching beyond that provided by the amendment calcium nitrate.

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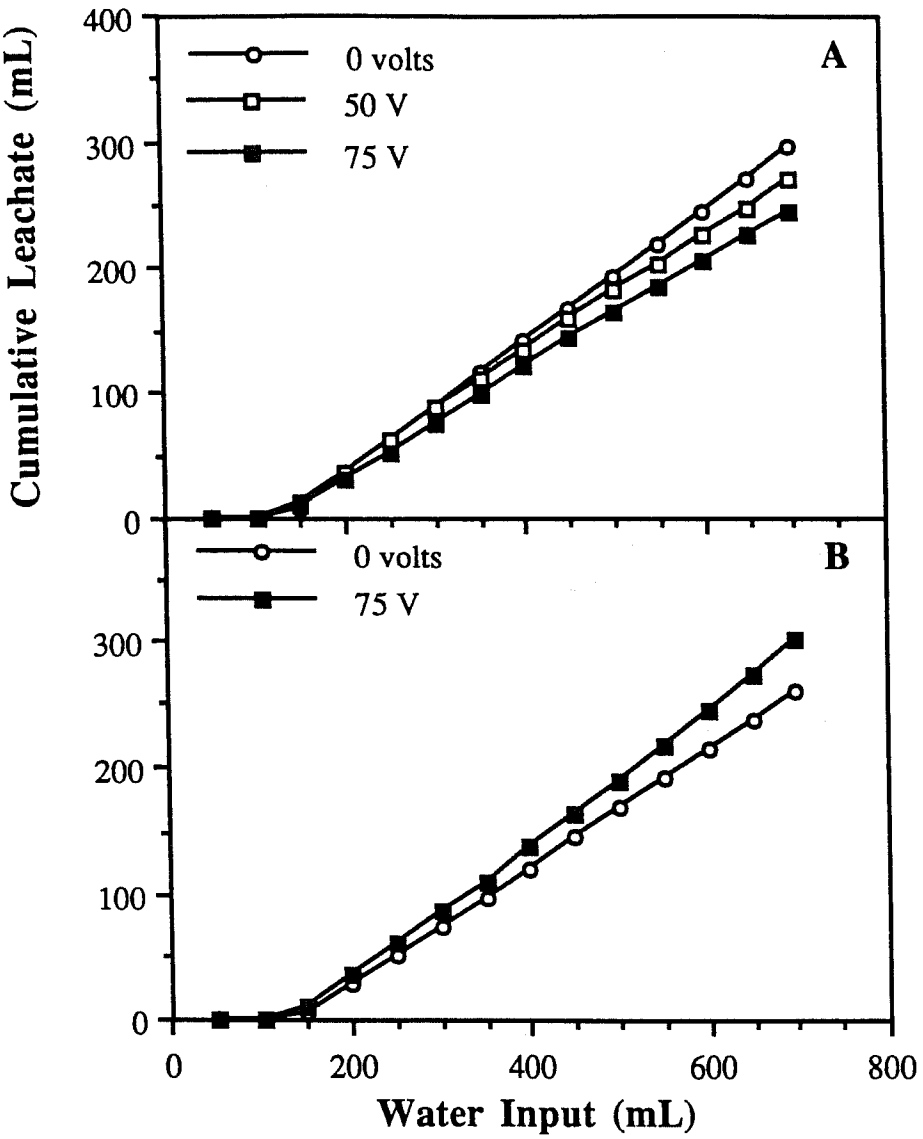

Figure 1. Cumulative leachate recovered during an incremental/bi-directional experiment with sand contaminated with NaCl.

A: Anode Drain (Drain 1 with 0 volts). B: Cathode Drain (Drain 2).

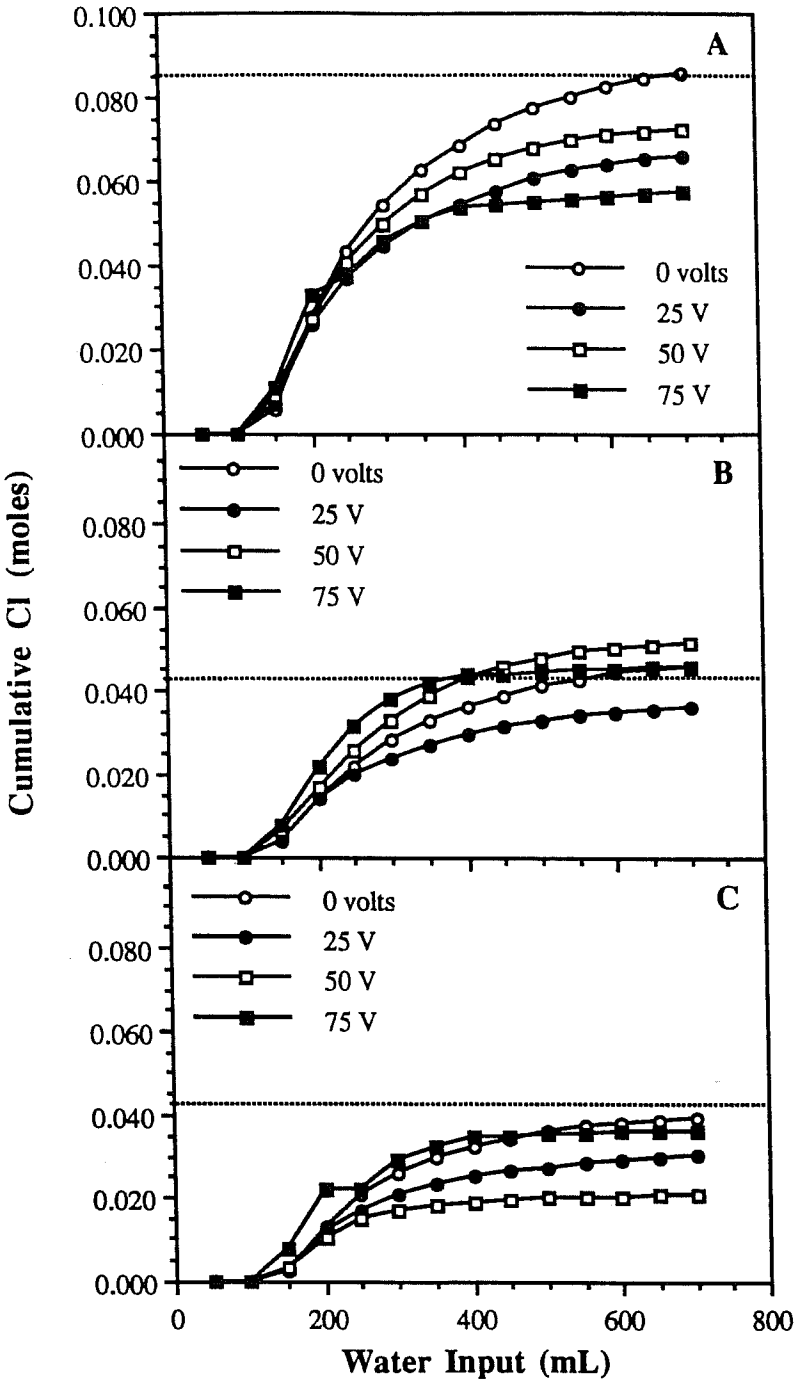

Figure 2. Cumulative chloride ion recovered during an incremental/bi-directional experiment with sand contaminated with NaCl (horizontal lines indicate amount added).
A: Total (both drains). B: Anode Drain (Drain 1 with 0 volts). C: Cathode Drain (Drain 2).

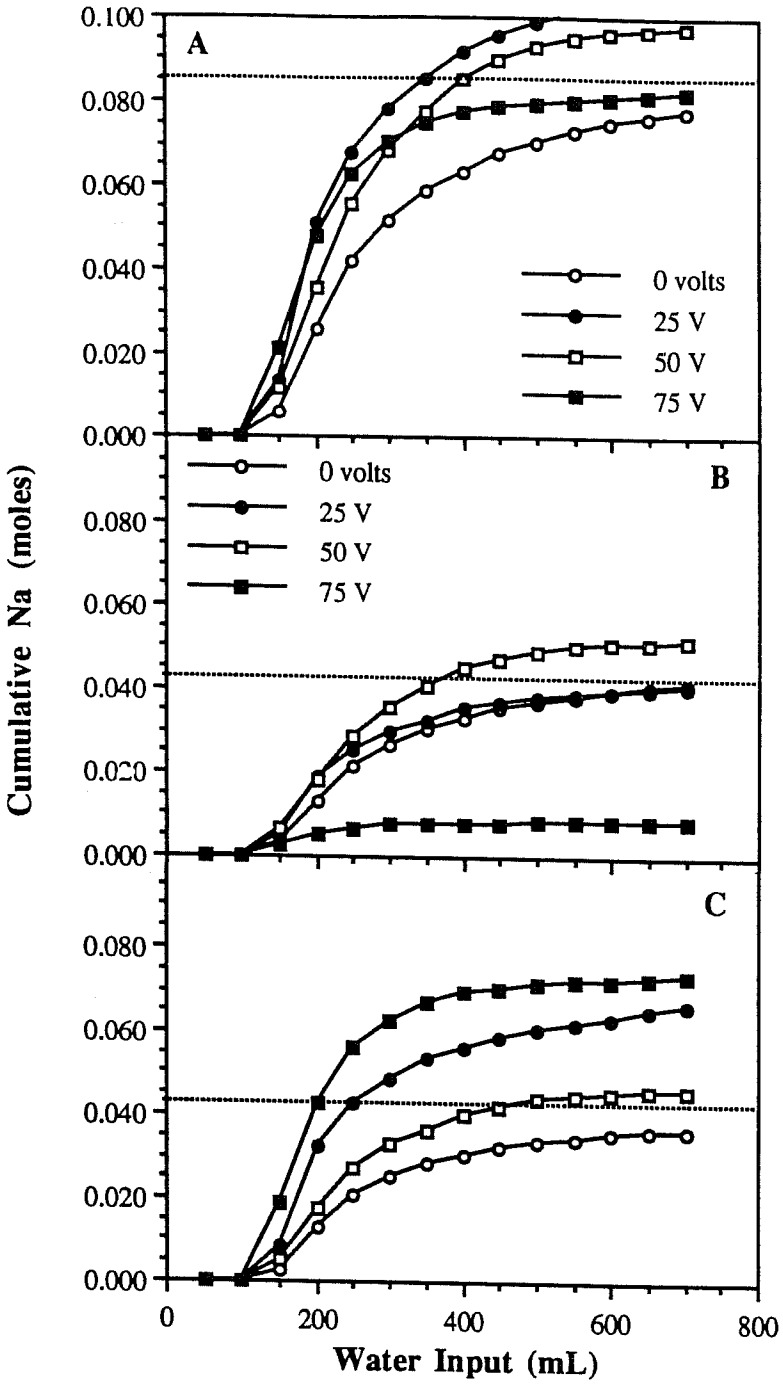

Figure 3. Cumulative sodium ion recovered during an incremental/bi-directional experiment with sand contaminated with NaCl (horizontal lines indicate amount added).
A: Total (both drains). B: Anode Drain (Drain 1 with 0 volts). C: Cathode Drain (Drain 2).

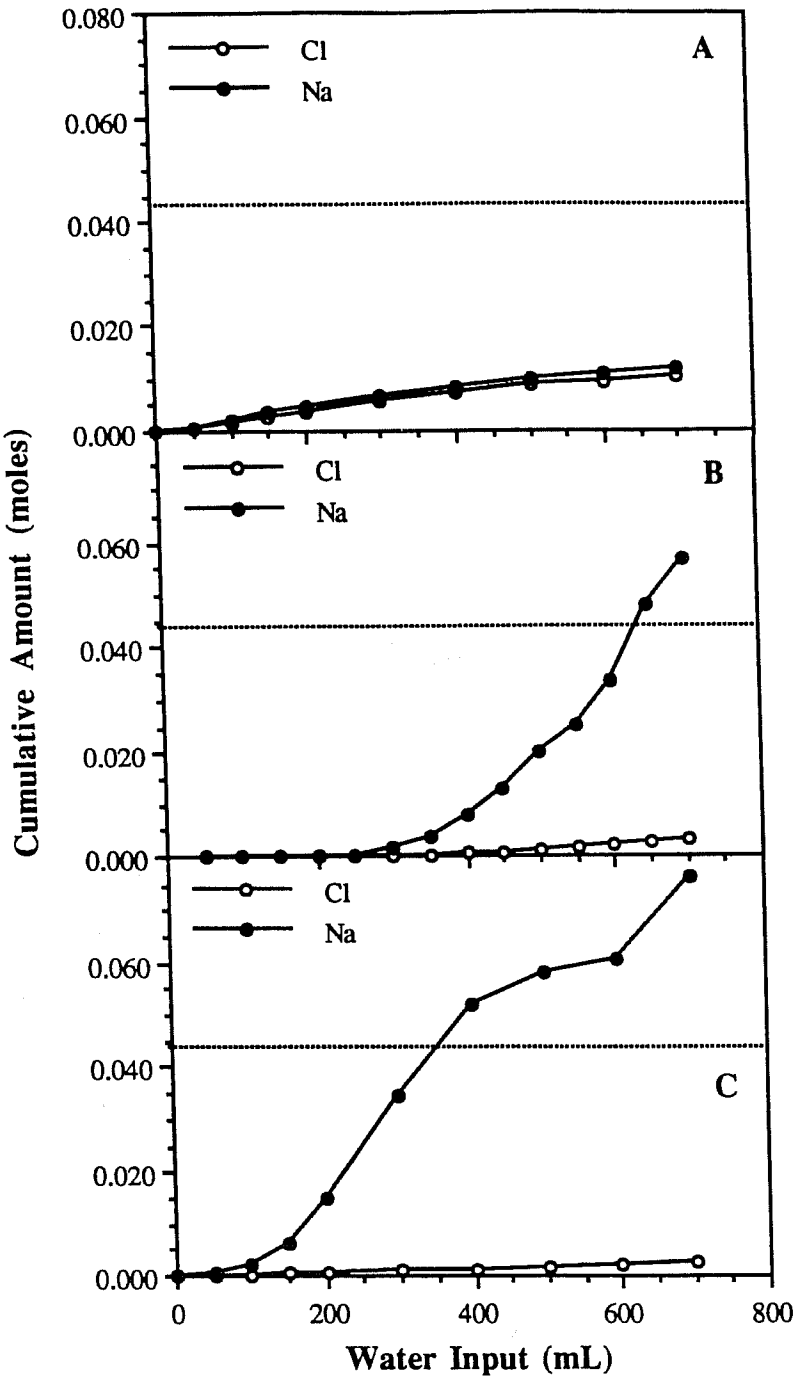

Figure 4. Cumulative ion amounts recovered during a continuous/uni-directional experiment with kaolin contaminated with NaCl (horizontal lines indicate amount added).
A: 0 volts. B: 50 volts, from Anode Drain. C: 50 volts, from Cathode Drain.

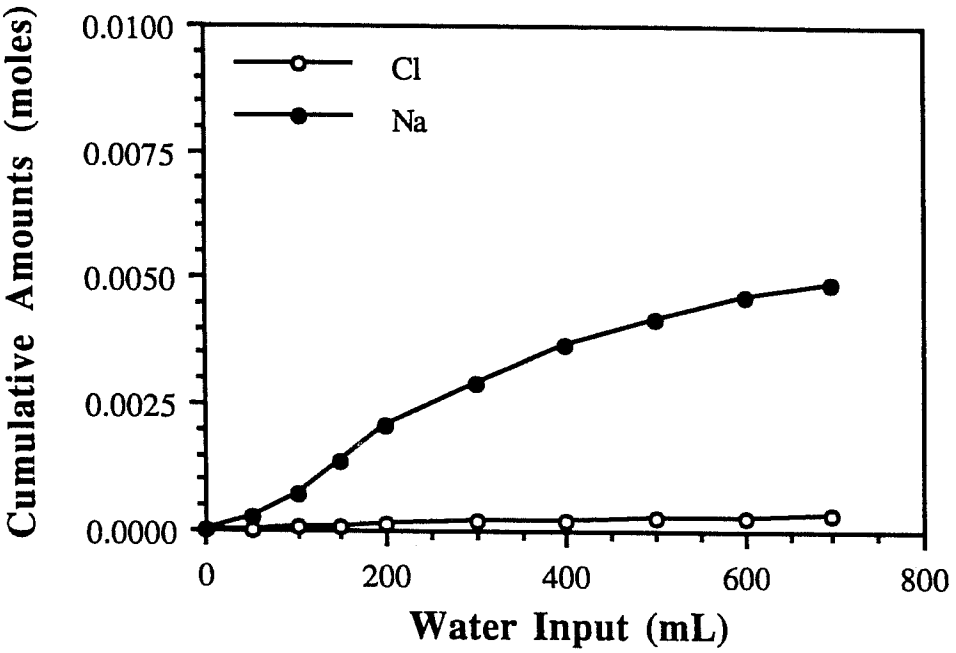

Figure 5. Cumulative ion amounts recovered during an continuous/uni-directional experiment with as-received kaolin (no NaCl added), 50 volts applied, and from Cathode Drain.

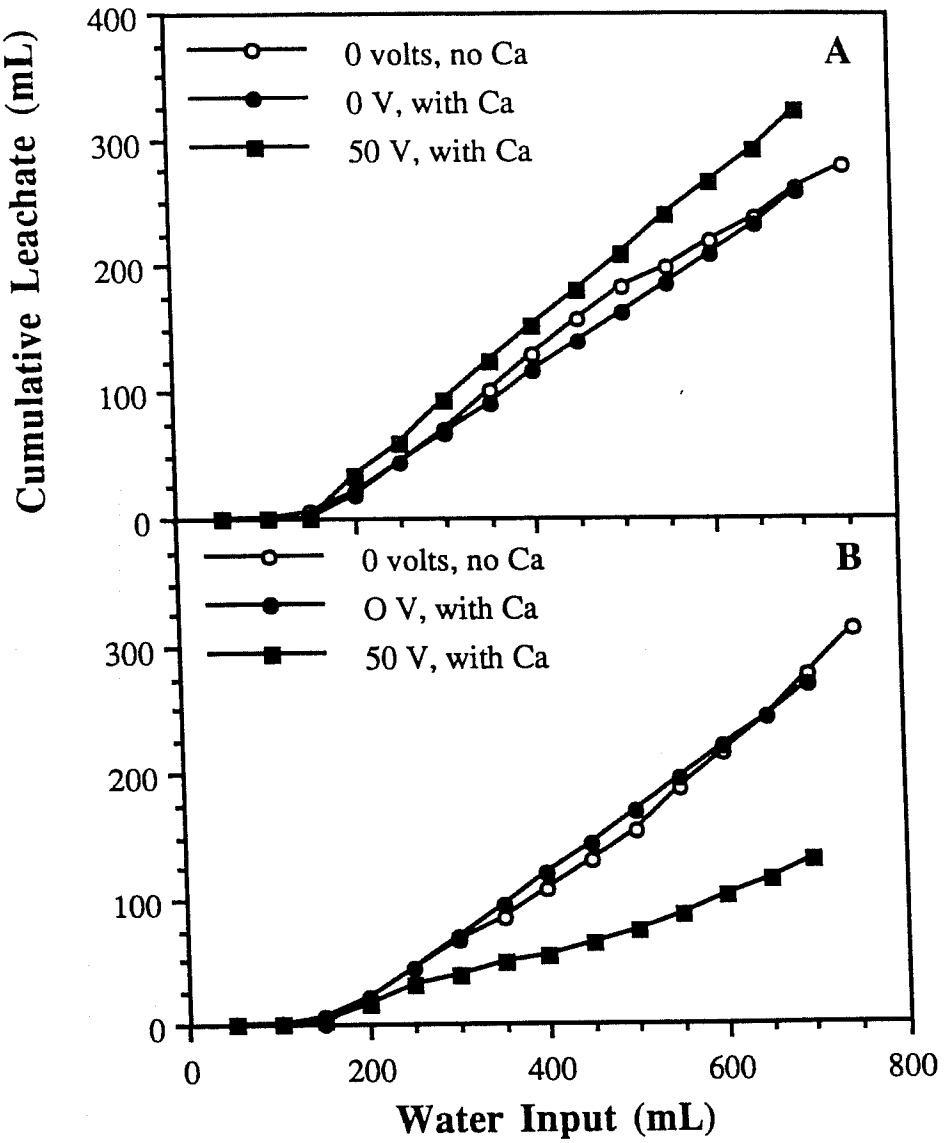

Figure 6. Cumulative leachate recovered during an incremental/bi-directional experiment with soil contaminated with NaCl. Calcium added as nitrate salt.
A: Anode Drain (Drain 1 with 0 volts). B: Cathode Drain (Drain 2).

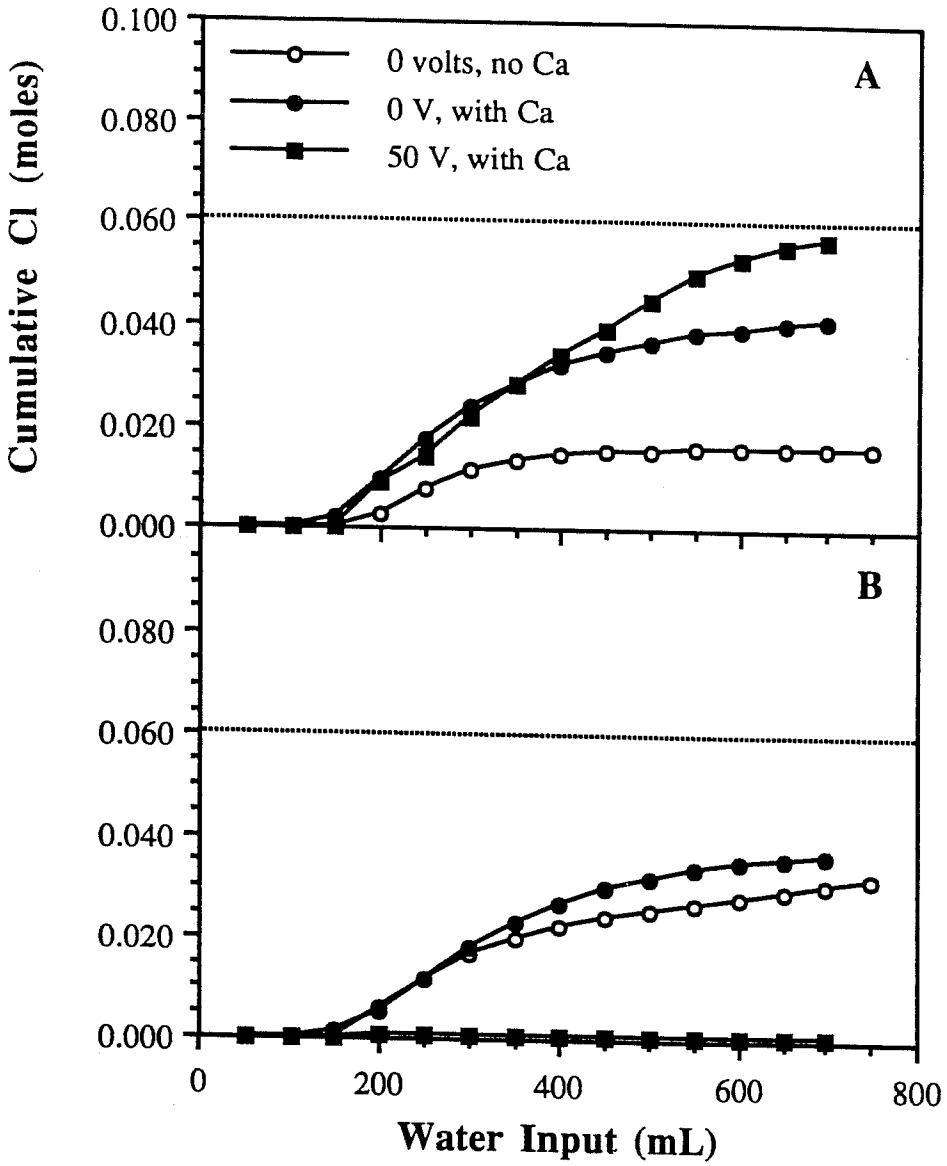

Figure 7. Cumulative chloride ion recovered during an incremental/bi-directional experiment with soil contaminated with NaCl. Calcium added as nitrate salt.
A: Anode Drain (Drain 1 with 0 volts). B: Cathode Drain (Drain 2).

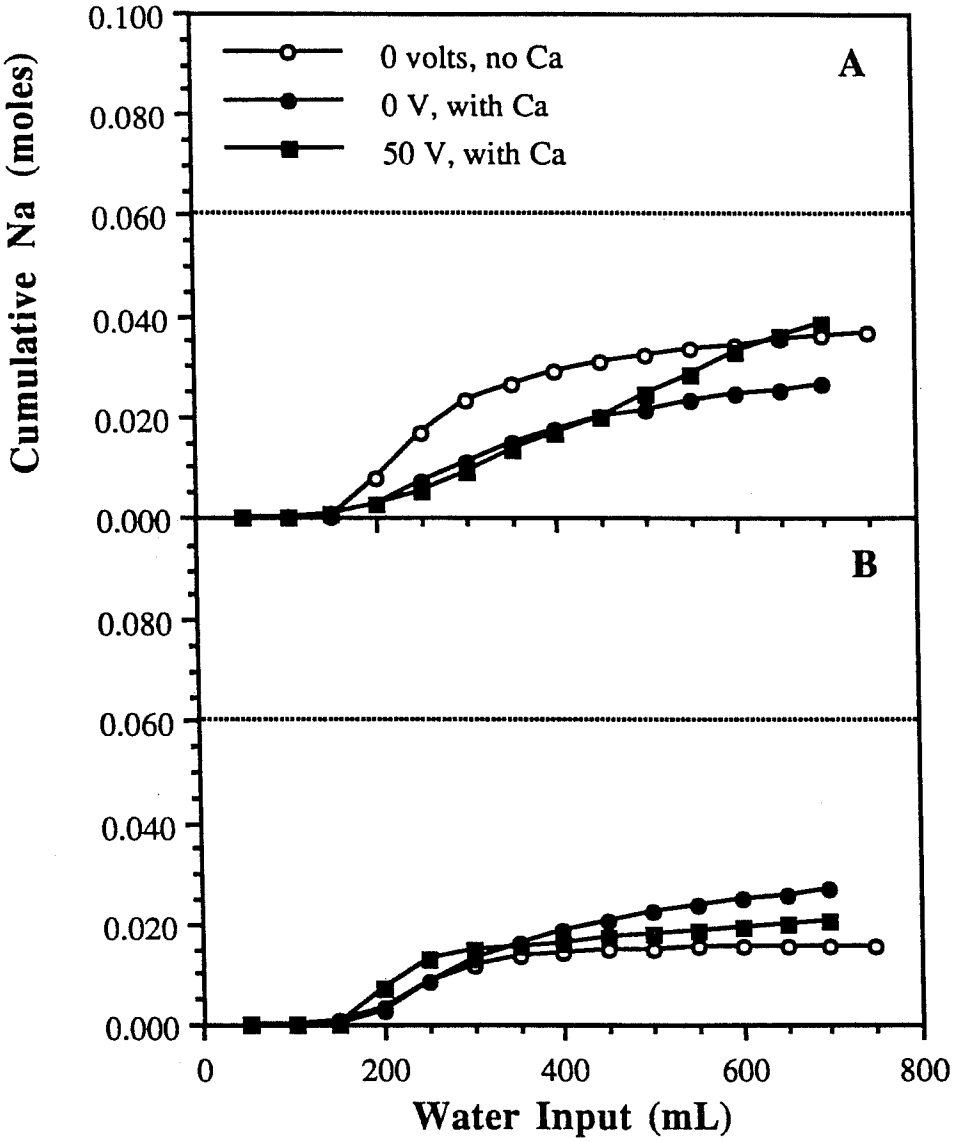

Figure 8. Cumulative sodium ion recovered during an incremental/bi-directional experiment with soil contaminated with NaCl. Calcium added as nitrate salt.
A: Anode Drain (Drain 1 with 0 volts). B: Cathode Drain (Drain 2).

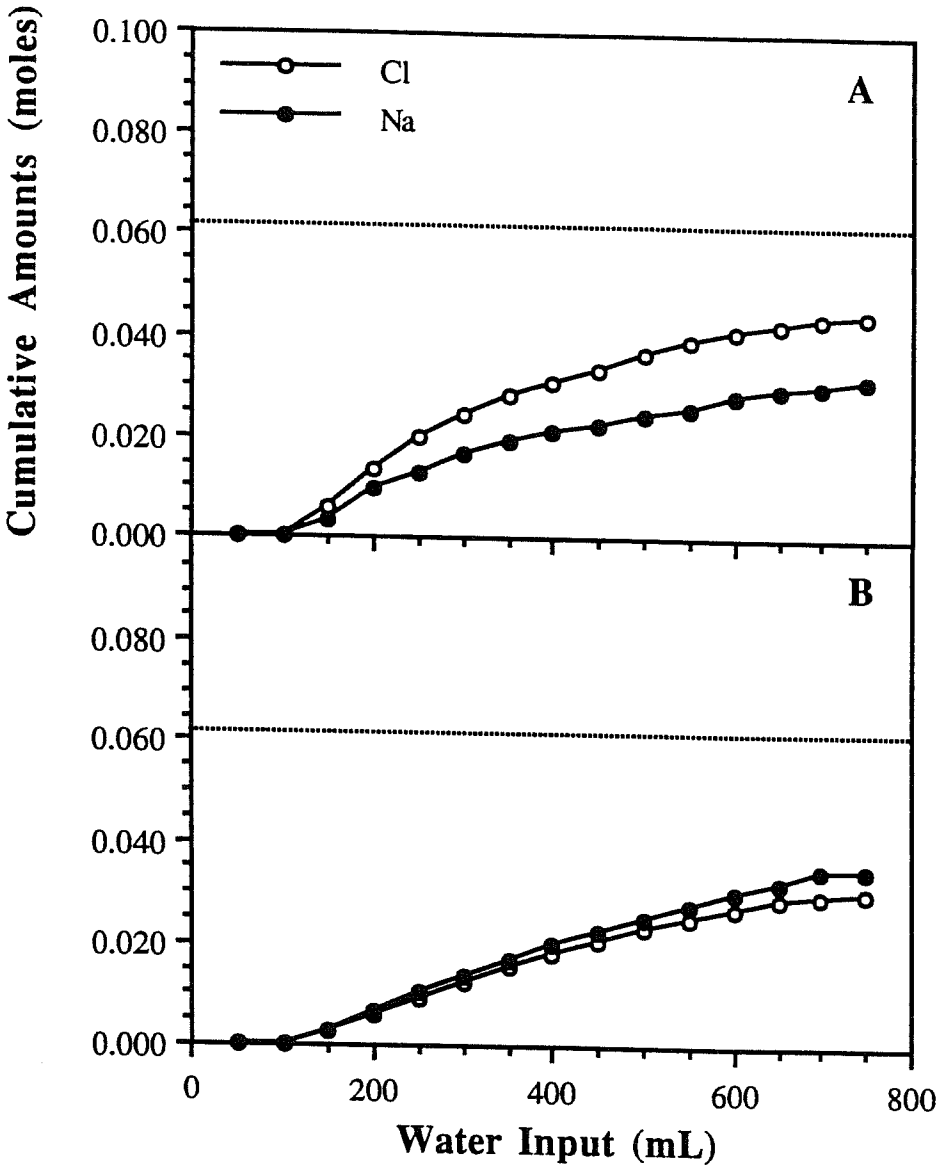

Figure 9. Cumulative ion amounts recovered during a continuous/uni-directional experiment with soil contaminated with NaCl (horizontal lines indicate amount added).
Calcium added as the nitrate salt.
A: 50 volts, from Anode Drain. B: 50 volts, from Cathode Drain.

The Biological Alternative: An Environmentally Safe Treatment to Lower Pressure and Reduce Problems in Saltwater Disposal and Water Injection Wells

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ABSTRACT

Saltwater disposal and water injection wells are prone to experience a reduction of injectivity caused by oxygen, iron sulfide, iron oxide, calcium carbonate, and oil carryover, to name a few. In the past a variety of approaches have been used to combat these problems including skimming, filtering, and chemical treatment.

This paper will present an environmentally safe biological approach to reduce water injection/disposal pressure and common problems associated with the operation of saltwater disposal and water injection wells. A description of mechanisms and treatment strategies will be provided and successful case histories will be presented to illustrate that the process is safe, effective, and affordable.

INTRODUCTION

Reinjected and disposed water from producing wells usually carries a variety of impurities, like oil and iron sulfide, that can slowly deposit and accumulate in surface water injection lines, downhole tubing and in the near-wellbore area of water disposal and injection wells, causing a gradual loss of injectivity. The microbiological process described in this paper has been used to slowly remove these accumulations and inhibit their ability to re-deposit.

In many oilfield production operations, a large amount of water is produced in addition to the oil. The oil and water must be separated from one another so that the produced water can either be reinjected into the producing formation to push more oil out of the ground, or pumped into subsurface water reservoirs for disposal. Since separation equipment lacks complete efficiency, it is inevitable that a small percentage of oil will not be removed from the water.

Consequently, oily water exiting the separation equipment is pumped to water holding tanks and ultimately reinjected or disposed into subsurface geologic formations via wells.

The problem is that the near-wellbore area of the geologic formation behaves like a filter to strip oil and other impurities from the water. Over time, these materials tend to accumulate in the near-wellbore, reducing permeability to a point that it becomes necessary to begin forcing the fluid into the formation with high pressure pumps. As permeability deteriorates with time, the pump pressure required to maintain the desired disposal/injection rate continues to rise toward inefficient or dangerous levels.

A microbiological process has been developed that uses the natural dynamics of water injection/disposal systems to help reduce the problem of line and tubular clogging, and of skin damage in subsurface formations. The primary components of this microbial system include a mixed community of naturally-occurring, dry powder hydrocarbon-utilizing microorganisms and special dry granular inorganic growth stimulants. The microorganisms have been tested and determined to be safe as they pose no threat to humans or the environment. The inorganic nutrient is simply a special fertilizer blend that poses no greater threat to humans or the environment than those associated with common lawn fertilizers and should, therefore, be handled with the same care. Once hydrated, the microbes and inorganic nutrients can be added to the water holding tanks or injection wellhead. By so doing, the water holding tank begins to function as a bioreactor, where the microorganisms feed on the carried over oil, converting it to a water soluble chemical surfactant by-product. The continuous process of converting oil to biosurfactant in the water holding tank is advantageous for several reasons:

- less oil is available to be pumped down injection/disposal wells
- surfactant helps reduce interfacial tension between oil and water droplets so they can more easily separate from one another in water holding tanks
- adding surfactant to water helps decrease friction between water and injection lines, and downhole tubing
- surfactants help remove oil and precipitated iron sulfide from water injection lines, downhole tubing and the near-wellbore formation

In addition to their role as surfactant producer, the microbes also serve another purpose. Since they reside in water, they are eventually pumped into the subsurface formation where they will contact the oily sludge buildup in the near-wellbore, recognize it as a food source, metabolize it, and remove it. The resulting permeability improvement provides for easier fluid entry into the formation, lower pump pressure, less wear and tear on equipment, and increased well life.

Additionally, since the microorganisms are of the aerobic and facultative type, they will scavenge dissolved oxygen from the system and use it in the oil metabolizing process, helping to reduce the tendency for the formation of iron oxide. A diagram of this process is presented in Figure 1.

BACKGROUND

Many commercial projects have been conducted in both water disposal and injection wells to quantify the effectiveness of the microbiological process at improving water injectivity. This paper will provide specific information on three projects, labeled Case Histories 1 though 3, including pre-existing operational problems, pre-treatment evaluation, treatment procedures, monitoring and evaluation, and results. These case studies are representative of what can be expected when employing this process.

PRE-MICROBIAL TREATMENT STUDY

Each case history in this report was pre-screened for compatibility and quality of field data. Prior to beginning the projects, representative samples of injected/disposed fluids were collected and tested for compatibility with the hydrocarbon-utilizing microorganisms. Pertinent field data was collected and studied, so that treatment strategies could be designed.

When applicable, historical water injection/disposal rate and pressure data was studied to establish the base-line for expected future rate/pressure relationships without the affects of the microbiological process. Also, pre-treatment operations data like filter changing frequency, chemical usage, frequency of acid jobs, etc., was determined so that any improvement in operational routine could be detected after microbial treatment began.

CASE HISTORY #1

A single water injection well within a waterflood unit located in Johnson County, Wyoming was treated to lower injection pressure. The zone being flooded was the Curtis sandstone formation which exists at a depth of approximately 900 feet from surface. The primary goal of this project was to microbially lower water injection pressure by removing suspected oil and iron sulfide deposits from the near-wellbore area of the pilot injection well.

Tabular historical water injection rate and pressure data was used to create graphs that would be used to detect any changes in injectivity after the microbial

project began. At the time the project began, approximately 700 barrels of water per day were being injected at a pressure of 830 psig.

The first microbiological injection was performed in July 1993. In order to keep the pilot injection well isolated from the remainder of the field, a 90 barrel biological solution was blended in a pump truck and pumped directly into the tubing of the water injection well as opposed to inoculating the water holding tanks at the central injection facility. Immediately after pumping the 90 barrel biological solution, the injection well was returned to normal injection in order to displace the biological materials into the reservoir. This treatment procedure was repeated once a month for a period of six months.

During the six month project, the 700 barrel per day water injection rate remained constant. Injection pressure, however, gradually decreased throughout the project and averaged 40 psig lower than the 830 psig starting point. The greatest reduction of injection pressure was observed in November and December 1993 with pressures averaging 50 to 70 psig lower than the pre-microbial level. Since no mechanical changes were made to influence injection pressure, it is believed that the hydrocarbon-utilizing surfactant-producing bacteria removed near-wellbore damage which pre-existed the microbial project, allowing for easier fluid entry into the reservoir. A rate/pressure graph is presented in Figure 2.

CASE HISTORY #2

Two saltwater disposal wells located in Upshur County, Texas were treated to lower water disposal pressure. The disposal zones were the Tokio and Blossom water sands which are encountered at a depth of approximately 3,300 feet from surface. Produced water from several wells flows through a series of settling tanks, to a horizontal freewater knockout ("FWKO"), and finally to water holding tanks where it is suctioned and pumped down the two disposal wells. It is theorized that oil carried over with the water slowly accumulated in the near-wellbore of the disposal wells over time causing injection pressures to gradually rise and eventually exceed the 900 psig limit imposed by the Texas Railroad Commission.

Prior to beginning the microbial project, the two disposal wells were periodically "back flowed" in an attempt to purge the near-wellbore of the accumulated oily sludge and temporarily lower disposal pressure. Pure oil would flow out of the disposal wells during back flowing for a period of at least 24 hours before turning to water. In addition to back flowing, traditional chemical surfactant and acid, which were added to the settling tanks on a regular schedule, had little to no affect on disposal pressure.

The first microbiological treatments were performed in October 1994. At the time the project began, approximately 5,100 barrels of water per day were being injected into the Tokio disposal well at a pressure of 1,200 psig; and 5,600 barrels of water per day were being injected into the Blossom at a pressure of 1,100 psig. Once a month, a biological solution is added to each suction water holding tank without interrupting normal water disposal operations.

During the first five months of treatment, water disposal rate remained constant; however, disposal pressure slowly decreased and then stabilized at 875 psig at each well. This translates into a 20% reduction in pressure at the Blossom well and a 27% reduction at the Tokio well. Additionally, each well has been back flowed since beginning microbial treatment and the water has remained clear and without oil. It has been confirmed that no variable other than microbial could have caused the reduction in injection pressure. A rate/pressure graph for each well is presented in Figure 3 and Figure 4.

CASE HISTORY #3

A waterflood consisting of two water injection wells ("WIW") and one salt water disposal well ("SWD") located in Grant County, Kansas was treated with the microbial process. Approximately 2,000 barrels of water per day are injected into the two WIW's at 1,400 psig injection pressure. The injection water passes through two water holding tanks before it is pumped down the WIW's. Any water in excess of 2,000 barrels per day is pumped down the SWD. Sludge, consisting of iron sulfide, oil carryover and paraffin accumulates in the tubular equipment and the near-wellbore reservoir of the WIW's and the SWD to cause a reduction in injection/disposal rate and an increase in injection/disposal pressure. Prior to microbial treatment it was necessary to treat the water holding tanks regularly with chemical de-emulsifier and surfactant. Additionally, iron sulfide particles have been removed from the water stream by utilizing 50 micron filters at each WIW wellhead. In the past, all filters were replaced at least once a week due to the accumulation of oily, iron sulfide sludge. The WIW's and the SWD have also been acidized once every two years to remove oil and iron sulfide accumulations from the near-wellbore reservoir.

Hydrogen Sulfide (H_2S) gas generated by Sulfate Reducing Bacteria (SRB) contributed to corrosion problems at the unit before the microbial project began. The presence of SRB and iron sulfide has caused the disposed/injected water to have a black color and foul odor. No treatment program has ever been implemented for the H_2S problem.

The use of conventional chemical de-emulsifier and surfactant was discontinued prior to implementing the microbial project which began in May

1993. Once a month, a microbiological solution has been added to each water holding tank at the unit.

Since the project began, no conventional chemical de-emulsifier or surfactant has been used in the water holding tanks and no acid treatment has been performed at the WIW's or the SWD. Water injection has been maintained at a consistent rate, and injection pressure has been reduced 22% to 1,100 psig. Filter replacement at the WIW's and the SWD has been reduced from once a week to once every 30 to 60 days which translates into at least a 75% reduction in filter use. The concentration of H_2S present in the injection water has been reduced to non-detectable levels and the clarity of the water has improved dramatically. A significant reduction in paraffin and oily iron sulfide sludge deposition in the flowlines of the producing wells and in transfer lines between water holding tanks has also been observed.

ECONOMICS

The process is economical. On average, the cost of the microbial process is $0.005 per barrel of injected/disposed water.

CONCLUSIONS

1. This microbial process is easily applied to water injection/disposal wells to lower pressure and results can be easily quantified.

2. On average, water injection pressure is reduced 20-25% after implementing the process with no negative affect on water injection/disposal rate.

3. This microbial process is inexpensive, usually costing about $0.005 per barrel of injected/disposed water.

4. No increase in injection/disposal pressure or decrease in injection/disposal rate have ever been observed as a result of microbial treatment.

5. This 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 Operators of these projects.

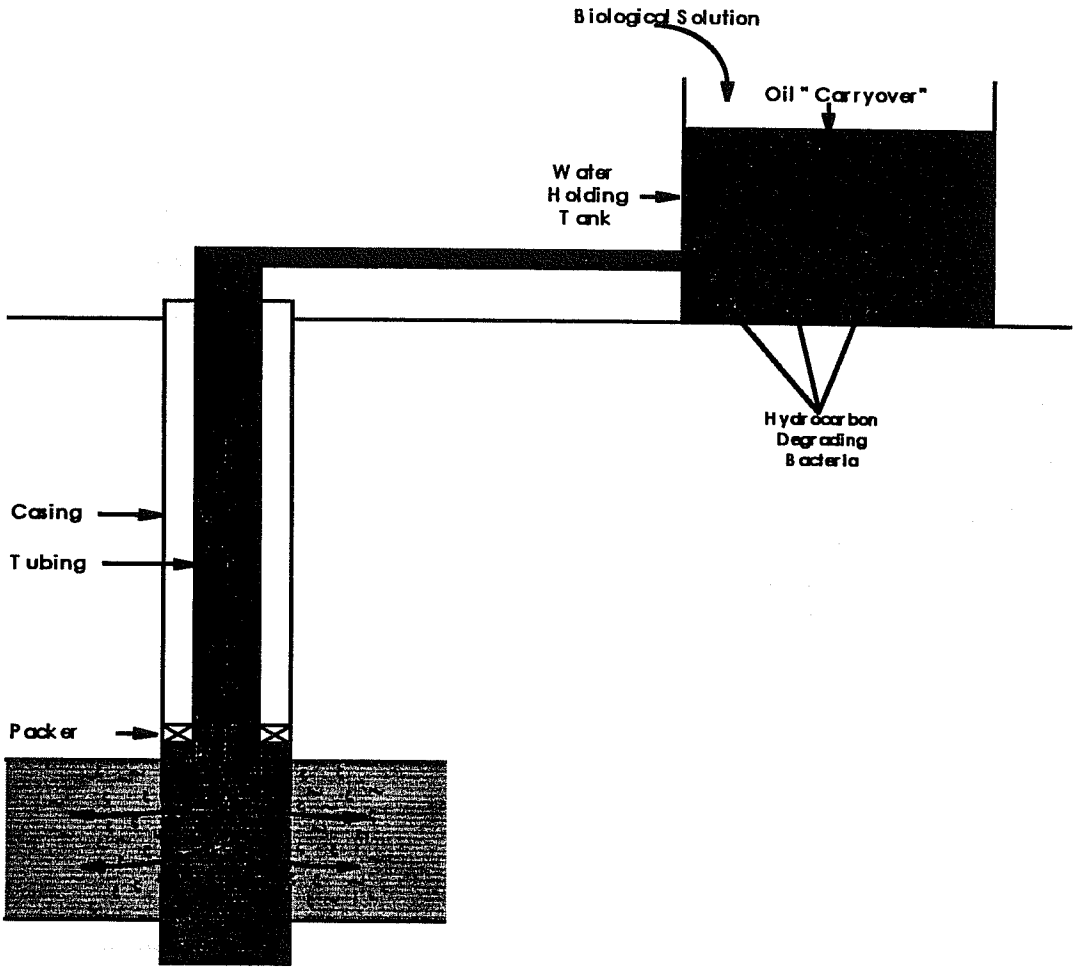

Figure 1. Schematic diagram of microbial treatment in saltwater disposal/injection wells.

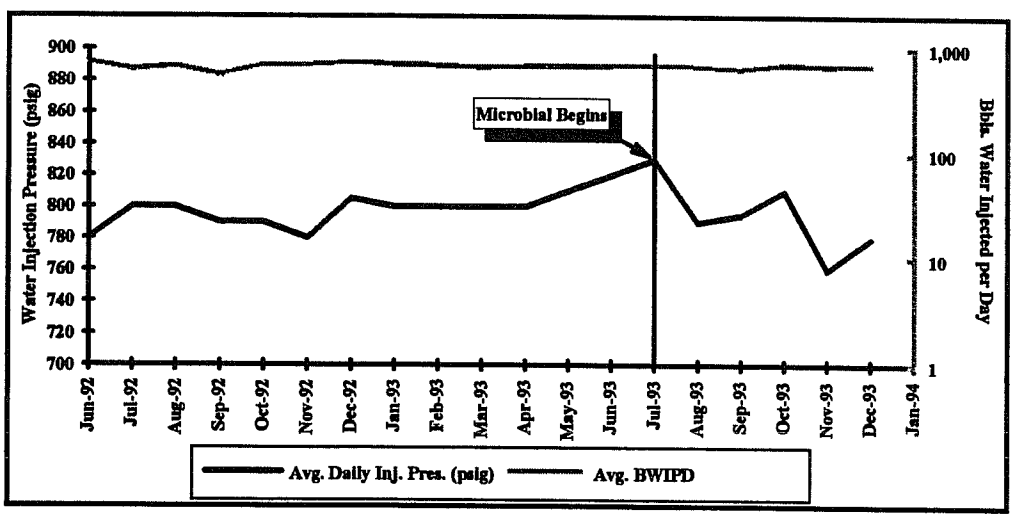

Figure 2. Curtis sand water injection well rate vs. pressure graph.

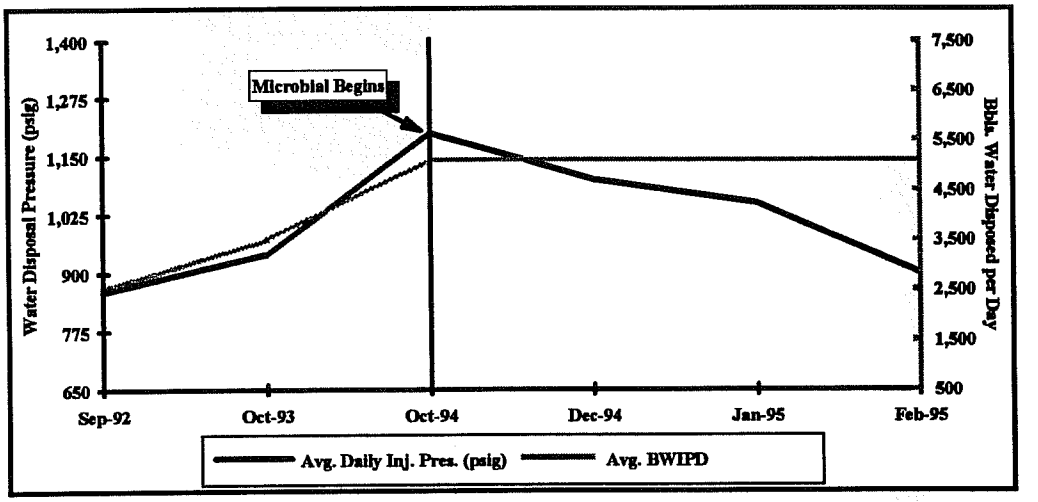

Figure 3. Tokio sand saltwater disposal rate vs. pressure graph.

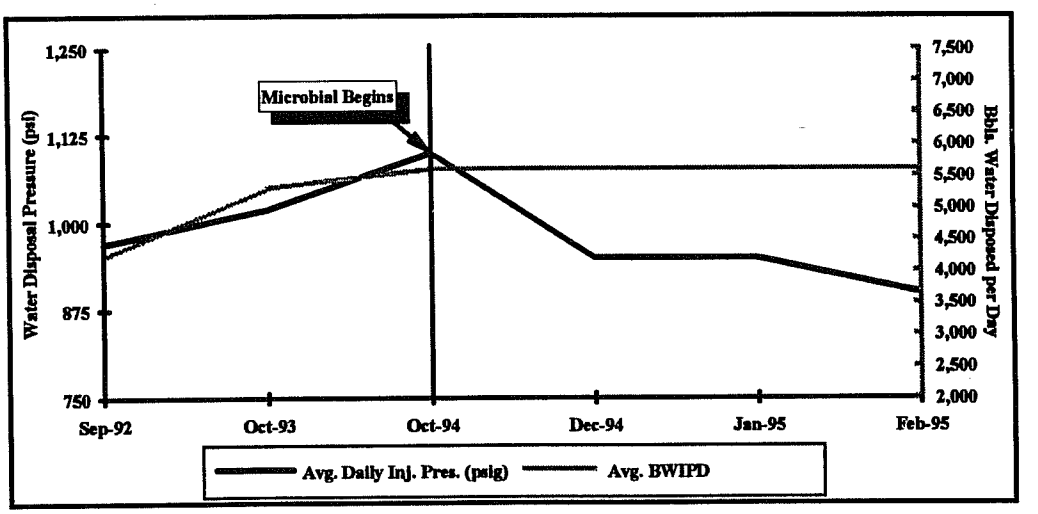

Figure 4. Blossom sand saltwater disposal rate vs. pressure graph.

A Cost-Effective Method of Performing Preliminary Assessments of Oil Field Brine Contamination: A Case Study

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Abstract

Winkler County, Texas, is located in a region of West Texas which has a water shortage. Inhabitants of the county rely on the Cenozoic Pecos Alluvium as their only source of water. Oil field brine disposal pits have contributed to the decline of water quality in the area. More than 10 billion barrels of brine were disposed of in unlined evaporation pits in Winkler County from 1920 to 1969.

To determine the impact of brine disposal, an assessment was made to:

1. Ascertain the impact on groundwater

2. Locate potential areas of high risk prior to any fieldwork in order to minimize field expenses over an area greater than 50 square miles

This was accomplished using contemporaneous reports, maps, and historical aerial photography. These data were input into a desktop geographical information system (GIS), subjected to geostatistical analysis, and kriged, producing brine contamination maps with error variance maps. Geochemical mapping was also performed.

The kriged maps show the migration of brine in the aquifer and indicate several areas in the county that may be at risk. The error variance maps indicate the degree of map reliability. These areas were targeted for field sampling, saving considerable field effort and expense.

INTRODUCTION

Winkler County, Texas, is the easternmost Texas county bordering the southern New Mexico state line (see Fig. 1). This geographic area is one of the major regions with a water shortage in Texas. According to 1995 Bureau of Census statistics, the county is sparsely populated with only about 11,500 inhabitants. Most of the county's inhabitants live in two cities: Kermit, population 9,289, and Wink, population 1,553 (see Fig. 2). The primary industries of this county are agriculture and petroleum services.

The inhabitants of the county rely on the Cenozoic Pecos Alluvium aquifer as their only source of potable water. The high ratio of evaporation to precipitation (lake evaporation is 76 inches/year; precipitation is 11.11 inches/year) results in the loss of any precipitation retained in the upper few inches of soil due to evapotranspiration. Aquifer recharge, measured in acre-inches, is less than 1 or 2 acre-inches/year. The increasing water demand, estimated to be 7,062 acre-feet by 2010, will place some strain on the water resources of the area. The irrigation demands of adjacent Ward County are responsible for a decline in the water table in southern Winkler County.

Oil field operations in the county during the late 1920s through the 1960s contributed to the decline of water quality in the area. Historical records show that Hendrick field (see Fig. 3) in Winkler County, one of the giant oil fields of Texas, has suffered water encroachment and disposal problems since its discovery (1–5). A map of the field (4) shows the size of the field at its maximum, containing more than 500 wells and covering an area of about 27 square miles (see Fig. 4).

A large proportion of the produced water from Hendrick field was disposed of in unlined evaporation pits until the state of Texas issued an order to cease disposal in open pits in 1969. Bignell (2) documents disposal pits as large as 40 acres (!) and the use of fissures in 640-acre dry lake beds to dispose of water. Draws were dammed, and salt water lakes were formed. Although the exact salinity of the waters in the disposal areas is unknown, Johnson (6) reported that the produced waters from Hendrick field ranged from 5,000 to 48,000 ppm total dissolved solids (TDS). Evaporation, although somewhat retarded by the film of residual oil floating on the surface of the pits, would increase the TDS concentration of the water escaping from the unlined pits.

Although the total amount of water produced from Hendrick field is unknown, Johnson (6) estimated that total field water production was about 11.7 billion barrels or about 1.5 million acre-feet. Thus, the possibility exists that a very significant quantity of water with high TDS concentration has escaped into the Pecos Alluvium aquifer and may have contributed to the decline in drinking water quality in Winkler Country.

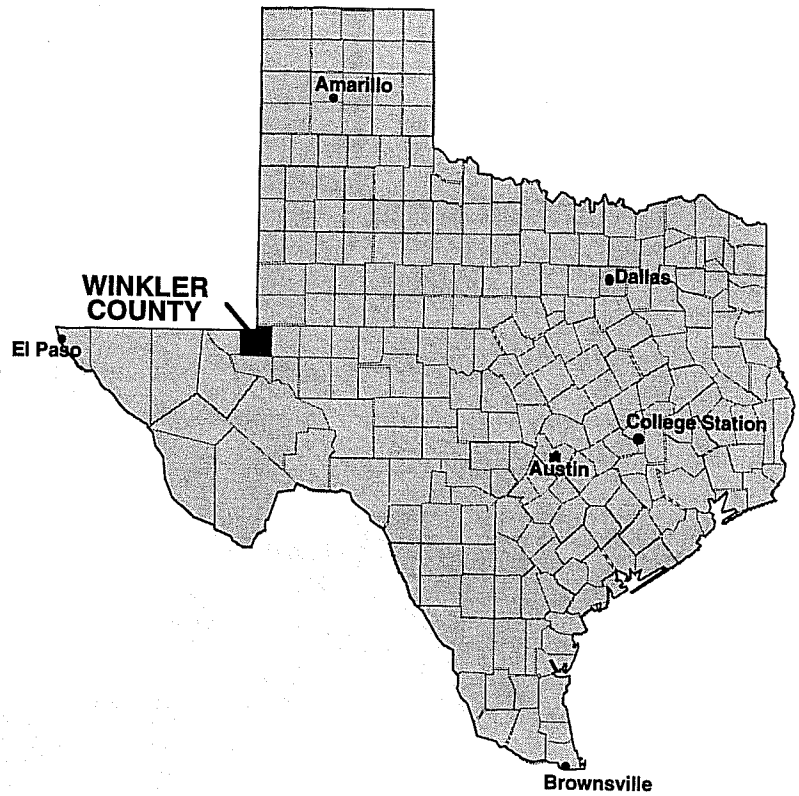


Figure 1. Location of Winkler County, Texas.

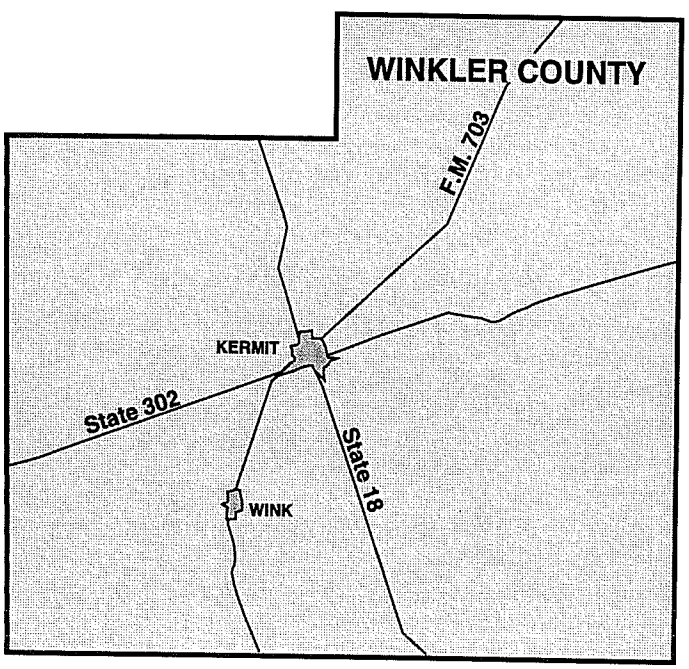


Figure 2. Cultural and transportation map of Winkler County, Texas.

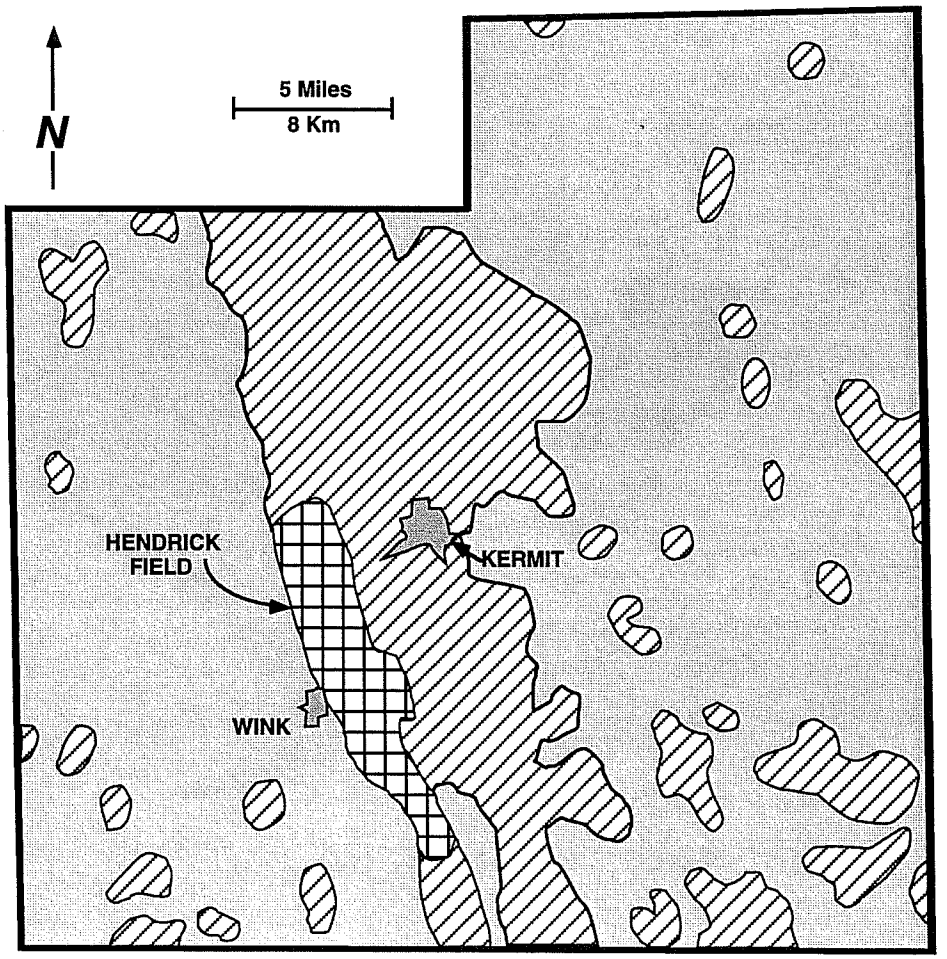


Figure 3. Petroleum-producing areas in Winkler County, Texas.

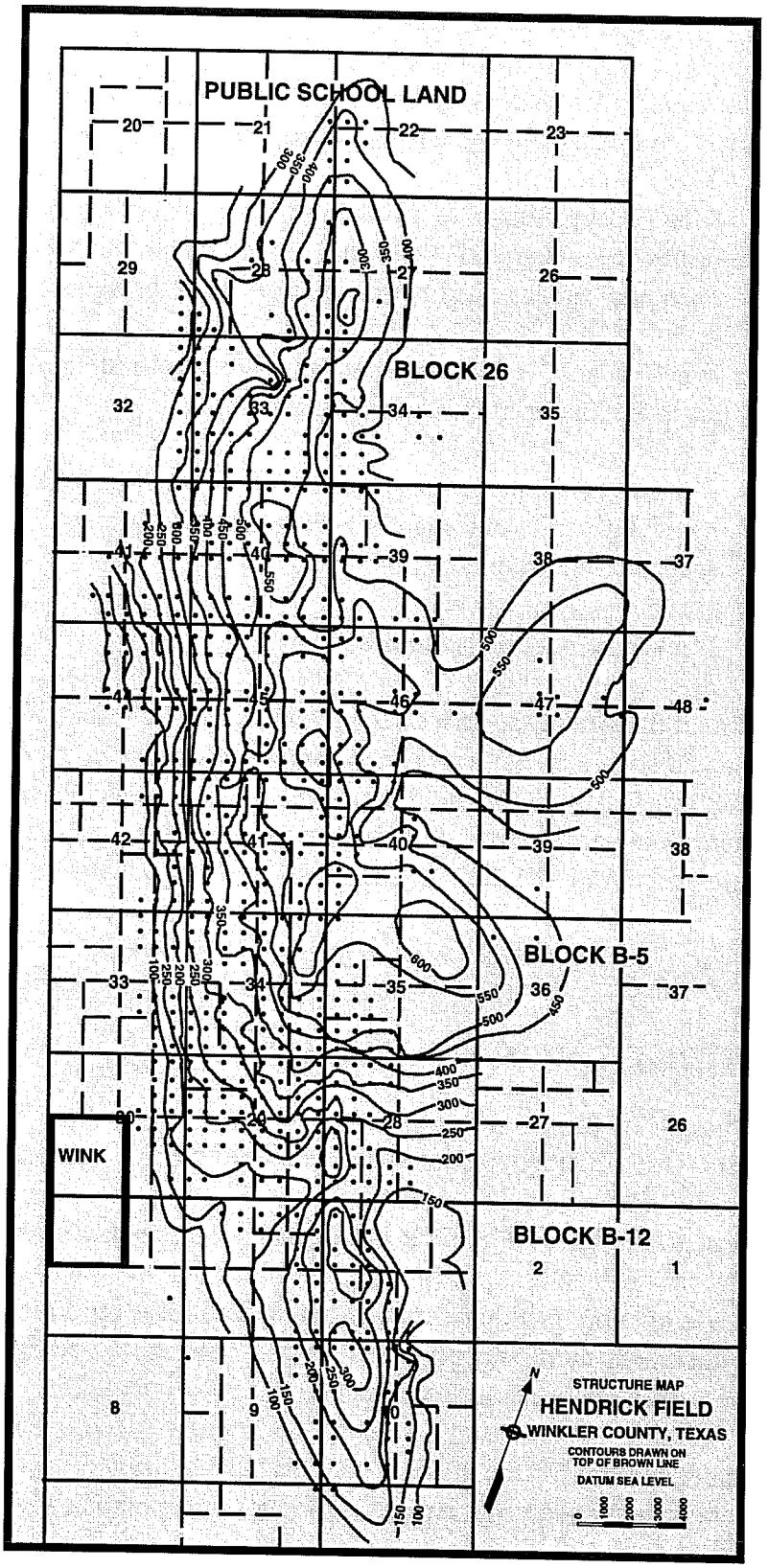


Figure 4. Structural map of Hendrick field, Winkler County, Texas (4).

PURPOSE OF THE ANALYSIS

To understand the impact of brine disposal operations on the Pecos Alluvium aquifer, an assessment was made to determine:

1. What, if any, impact to groundwater was caused by the disposal of brines from Hendrick field operations prior to the "no disposal in open pits" order issued by the state of Texas in 1969.

2. What, if any, effects or changes have occurred to groundwater since the "no open pit" order was issued.

3. If enough evidence exists to warrant field work to confirm or deny, by scientifically and legally accepted methods, the existence of a suspected environmental risk.

4. If no further action is required.

Because of the size of the area affected (estimated at the start of the project to be more than 50 square miles), it was necessary to locate areas at potential risk before any fieldwork to minimize field expenses. To help reduce expenses, only available public domain data were obtained to perform the analysis. The more expensive fieldwork would be based on the results of the analysis of the public domain data.

DATA ACQUISITION AND HANDLING

A summary of the operational practices and the petroleum geology of Hendrick field was obtained by acquiring and reviewing contemporaneous reports, maps, and other available published data. These reports ranged from the late 1920s through the 1990s. Photos in contemporaneous industry journals from the 1920s showed rigs, disposal pits, and typical field equipment. Historical aerial photography was obtained with dates ranging from the 1940s until present. These photographs document numerous pit locations and other field activities through time and represent an important data source (7).

An understanding of the surface geology and hydrogeology of Winkler County was obtained by acquiring and reviewing available reports and maps. The appropriate data from these sources were digitized and placed in a desktop (AutoCAD-based) geographical information system (GIS). Data captured included well locations, chemical concentrations, well identification numbers,

cultural features, surface geology, topographic maps, maps derived from aerial photographs, geologic maps, road maps, and other sources of cartographic data.

The GIS allowed the combining and display of maps to enhance and facilitate the analysis. Figure 5 shows the primary groundwater recharge areas in Winkler County (8). Figure 6 combines two maps: primary groundwater recharge areas and base of Pecos Alluvium Aquifer. The versatility and usefulness of a GIS is illustrated by allowing the program to construct perpendiculars to contour intervals, as shown in Figure 7. The perpendiculars, shown by arrows, indicate the direction of groundwater movement in the Pecos Alluvium during 1989.

The U.S. Soil Conservation Service has not done a soil survey of Winkler County. By correlating data in the GIS from a soil map of adjacent Ward County with a generalized surface geological map, soil associations with their permeability, shrink and swell capacity, and water retaining capacity could be inferred. These data could be used to estimate the rate of disposed-brine escape from unlined pits. Future groundwater modeling could also be performed.

Groundwater data for Winkler County, although sparse, were available through the Texas Water Development Board. A 1969 report (9) describes the only aquifer test in Winkler County. Although the test well did not fully penetrate the aquifer, the data from the test were used to obtain an estimation of the hydraulic conductivity of the Pecos Alluvium. Using geological descriptions of the alluvium, an estimate of effective porosity was made using methods of Fetter (10) and Dawson and Istok (11). This allowed the calculation of an estimated rate of groundwater movement of less than 50 feet/year, well within the range of typical groundwater velocities in arid environments with little recharge (10). All calculations were retained for future groundwater modeling purposes.

The low groundwater recharge rate in the area creates little driving force for the movement of groundwater. Thus, a well withdrawing water from the aquifer would overcome the natural hydraulic gradient and draw possible brine contamination from considerable distances.

Two published reports were found to contain sufficient data for analysis purposes (5, 12). Data from 30 wells in Winkler County were obtained from the first report; data from more than 100 wells were obtained from the second report. These data included location and depth of well or sampled interval, water levels, and chemical analyses of the water samples. These data were placed in the GIS.

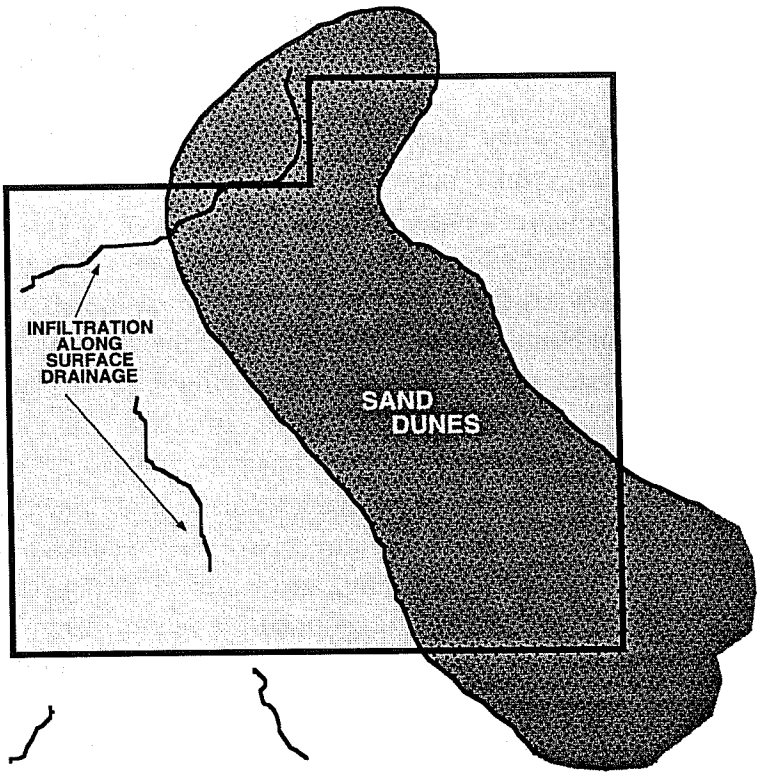


Figure 5. Primary groundwater recharge areas, Winkler County, Texas.

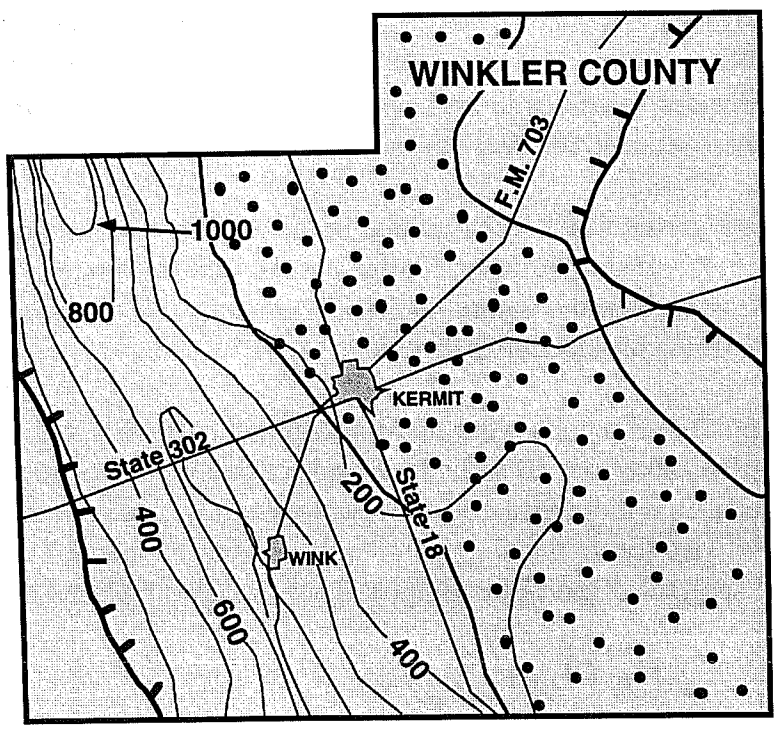


Figure 6. Primary groundwater recharge areas and base of Pecos Alluvium, Winkler County, Texas.

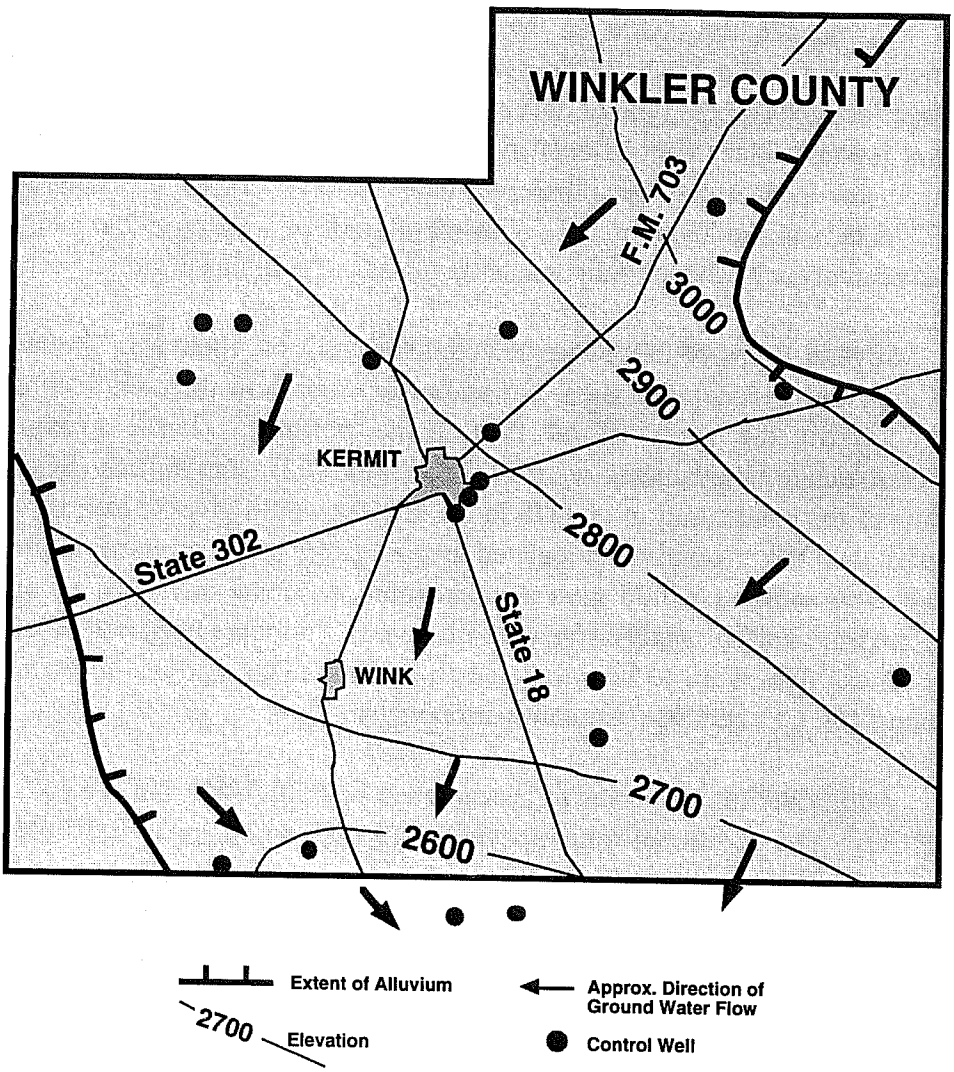


Figure 7. Altitude and direction of groundwater in Cenozoic Pecos Alluvium (1989), Winkler County, Texas.

DATA HANDLING

In accordance with standard GIS practice, data were stored in different layers (see Fig. 8). Two layers are essential in a GIS. The first is the geodetic control or survey control layer. The function of this layer is to provide a spatial reference system so that succeeding data are aligned with the reference system. The southwest corner of the county was selected as the arbitrary x =0, y = 0 reference point. The second layer is the base map. Once geodetic control is established, major features may be placed on the base map. The base map layer is the reference layer to the succeeding data layers.

The succeeding layers are the data layers. They consist of data essential for analysis and contain the attributes deemed critical. The placement of a data set in a layer depends on the type of data and how critical the data are to the decision-making process. Placement of data in layers are made during data encoding and input; however, data may be transferred between layers or to new layers at any time. The data in the layers may be viewed interactively on screen at a computer workstation or by hard copy plots made by plotter or graphics printer.

Several types of data were selected for analysis, including groundwater elevations and geochemical data. Groundwater data were selected according to Mast (13) for the study of oil field brine pollution. Three groundwater characteristics to be evaluated were TDS, chloride (Cl^-), and sulfate ($SO_4^=$). The analysis of the concentration of TDS in the aquifer would give an overall view of pollutants in the groundwater caused by oil field brine contamination. The chloride ion analysis would give a representation of the influence of oil field brine, and the sulfate analysis represents one of the characteristics of oil field brine. These data were to be subjected to geostatistical analysis and kriged to produce TDS, Cl^-, and $SO_4^=$ contamination maps.

Additional ionic species to be analyzed were Na^+, K^+, Ca^{++}, Mg^{++}, $CO_3^=$, and HCO_3^-. The additional ionic species were used to construct Stiff diagrams (14). The Stiff diagrams were placed in a separate layer in the GIS to be overlaid on the kriged contamination maps to compare or determine the nature of any possible brine contamination observed in the groundwater. Figure 9 shows three Stiff diagrams created during the study. The "hourglass" shape of the produced water is distinct from that of the groundwater.

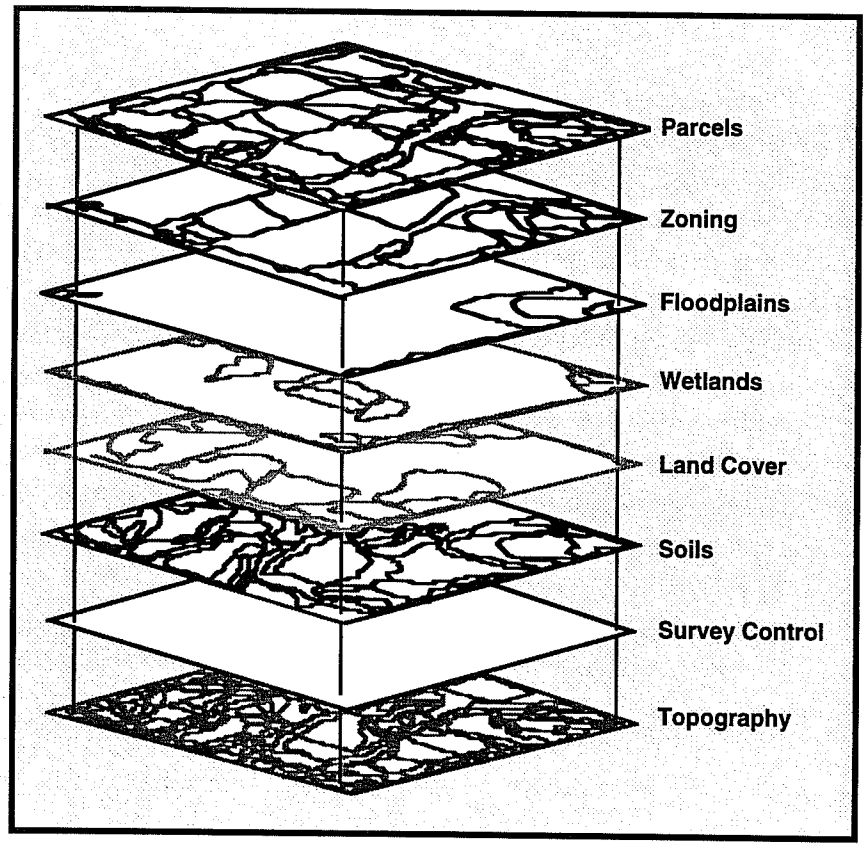


Figure 8. GIS data layers.

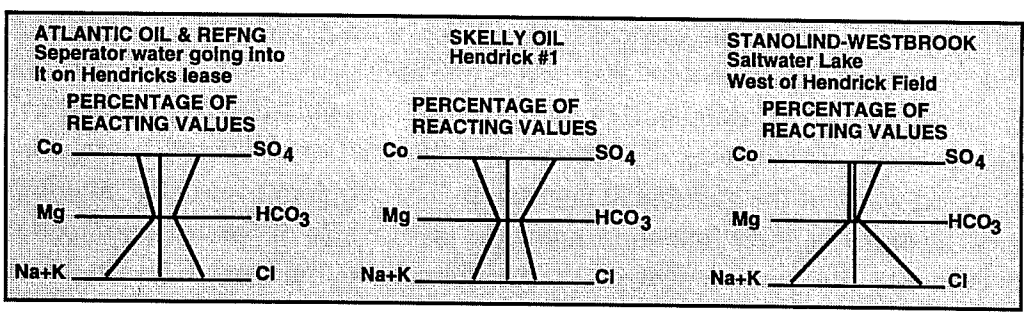


Figure 9. Stiff diagrams derived from the study.

GEOSTATISTICS AND KRIGING

The data sets containing the characteristics to be evaluated were selected for geostatistical analysis. The term "geostatistics" is applied to a special branch of applied statistics developed by Georges Matheron of the Centre de Morphologie Mathematique in Fountainbleau, France. Geostatistics can be defined as a technique or method for estimating or making inferences about quantities that vary in space or time. This is important in the field of geohydrology, where data typically varies not only in space, but also in observed values that change over time. Geostatistics measures similarity or dissimilarity between observations. Based on data and distance between observations, a statistical estimation of change or spatial variability can be made. Once the rate of change has been determined, it can be used to predict spatial values for locations where observations have not been made.

Spatial variability, particularly in geology or hydrogeology, is generally not purely random. A correlation exists between the spatial distribution and the changing magnitudes of the data undergoing analysis. The term "regionalized variables" is used for variables developing or changing in space and/or time and possessing a certain structure, where the term "structure" refers to the spatial correlation that is very different from one location to another. Any change in the regionalized variable can be statistically evaluated, and the rate of change or structure can be estimated. This is accomplished by calculating the semivariance, which is a measure of the spatial dependence between samples. The semivariance is calculated for different distances (called lags) and plotted as a semivariogram.

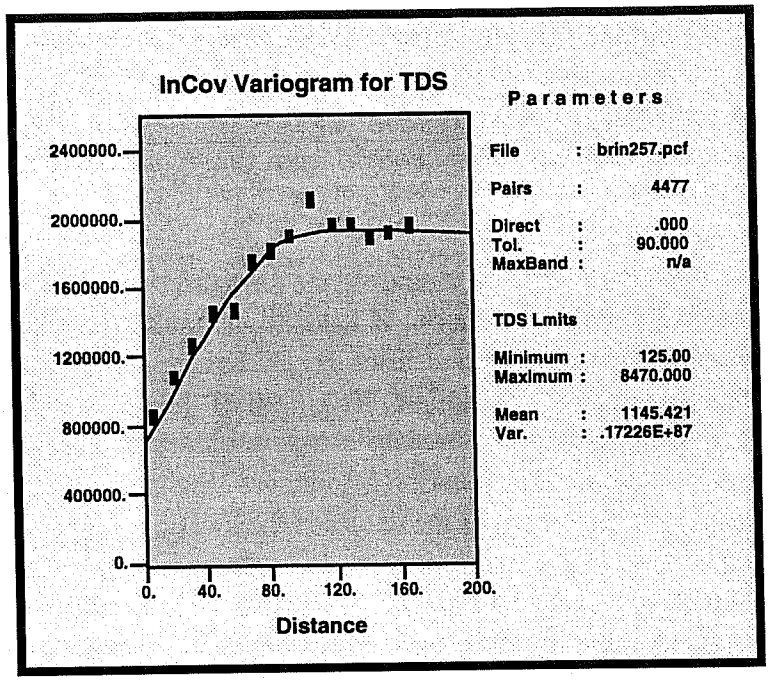
Once the semivariogram is obtained, "structural analysis" must be performed. This is the process of fitting a mathematical model to the semivariogram. This is not an easy task. To determine the model, one must know the exact size of the neighborhood of the data (neighborhood is defined as the region where *all* locations are related) and the drift of the variable (drift is the expected value of the variable at any point). The problem is circular: to compute the drift of the variable, one must know the precise size of the neighborhood, and to compute the precise size of the neighborhood, one must know the drift precisely.

According to Davis (15), finding the proper mathematical model is an art, requiring experience, patience, and sometimes luck. Structural analysis is a matter of interpretation as an infinite number of mathematical models will have the same "fit," and only one model is correct. Thus, fitting the proper mathematical model to the data is a subjective and interpretive choice that must be based on a "best

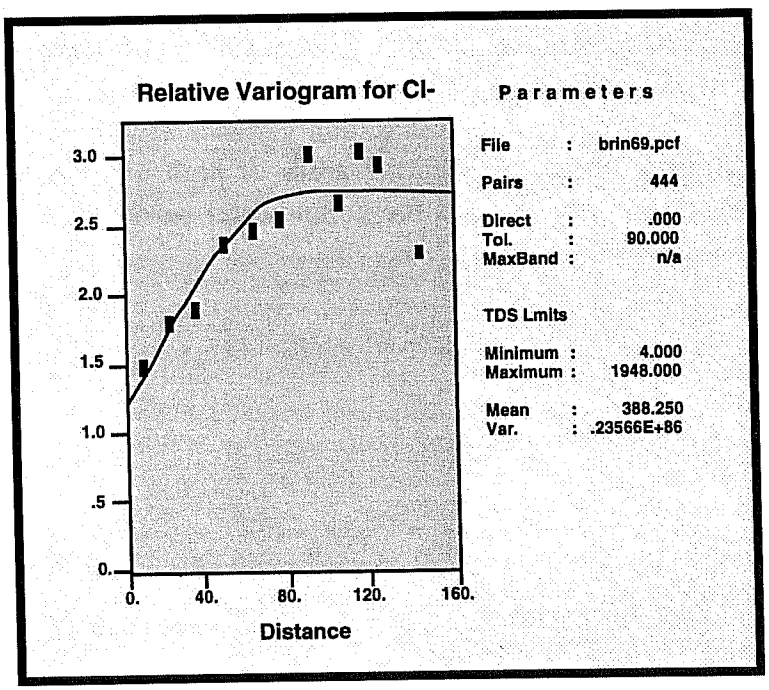
geological or engineering judgment." To determine the exact model requires extensive sampling. However, if this is done, there is no need to perform geostatistical analysis as the sampling has discovered all aspects of the site in question. Some variograms with models from the Winkler County data set are shown in Figure 10.

After a semivariogram has undergone structural analysis and a model has been applied to the data, the model is used to estimate values at any point by kriging. This procedure is named after D. G. Krige, a South African mining engineer who pioneered the technique. Kriging uses the semivariogram to find an optimal set of weights that are used to estimate values at unsampled locations. Since the semivariogram is a function of distance, the weights change according to the geographic arrangement of the data and the location under analysis. Kriging will estimate a *value and a range of probable values or confidence levels* for any unsampled location within the data set. Based on the data set, the true or actual value for an unsampled location may not be precisely what was estimated, but will have a better than 95% probability of being located within the range.

Because of the mathematical nature of the kriging process, the estimations derived are unbiased and considered a BLUE or best linear unbiased estimate (16). The unbiased nature of the estimation and the ability to obtain confidence values make the method useful for a wide variety of applications, such as estimation of transmissivity, piezometric head, and concentrations of solutes (contaminants) in aquifers. The estimation variance can be used to locate field data measurement points by locating areas of high uncertainty. Finally, the estimation variance can be used for groundwater modeling using conditional simulation techniques.



(a)



(b)

Figure 10. (a) TDS variogram nugget 700000, sill 1200000, range 99, spherical model; (b) variogram for Cl^-, nugget 1.2, sill 1.55, range 85, spherical model.

RESULTS

The kriged groundwater maps showing contoured TDS values and Stiff diagrams from the 1957 and 1979 data sets are shown as Figures 11 and 12, respectively. The 1957 map (see Fig. 11) shows a TDS plume with a concentration higher than 3,000 mg/liter about 6 miles long between the towns of Kermit and Wink. The error variance results from kriging show high statistical data reliability in the data from this area.

A map of the 1957 water table elevations shows a groundwater mound in this area. This is interpreted as large amounts of produced water escaping from unlined pits into the alluvium in such quantities as to raise the water table by about 20 feet. This area correlates well with the highest structural contours of Hendrick field and would be a focus for water extraction due to waterflooding that was underway in 1957. The wells located in this area would be the last ones to be abandoned and would recover the most water during the life of the field. Aerial photographs taken in 1964 show many abandoned and operating pits in this area.

The Stiff diagrams show that the ionic concentrations in the groundwater within the mapped plume are similar to the produced waters from Hendrick field. The hourglass shape is unmistakable. Waters uncontaminated by brine have a distinctive "arrowhead shape" and can be seen in the central portion of the map. Of importance is the position of the 1,000 mg/liter contour (the maximum allowable TDS concentration in drinking water), immediately west of Kermit and immediately east of Wink. The movement of this contour over time is important.

A high concentration of brine appears northwest of Wink. Historical records and aerial photographs show that Monument Draw, a groundwater recharge area north and west of Wink, was dammed, and a salt water disposal lake was created in this general area. The error variance results from kriging show a high statistical data reliability in the data from this area.

The 1979 data, acquired 10 years after the "no pit" order, shows the brine contamination has reduced and dispersed since 1957. However, the kriged map (see Fig. 12) shows that a substantial plume about 6 miles wide and 12 miles long exists with TDS levels as high as 2,500 mg/liter. It is apparent that the plume is migrating over time.

The 1979 TDS map shows that the brine plume west of Kermit is migrating up-gradient, toward the city. The plume is perhaps drawn by the pumping of the city water supply and other wells reversing the regional hydraulic gradient. Error variance data shows that this data is statistically reliable.

Because of the level of disposal operations in this area and the character of the soils, a large amount of residual salts or leachate are likely present. Murphy et al. (17) showed that saline leachate in soils under oil and gas brine ponds in semiarid areas were sources for groundwater pollution. Murphy et al. showed that the amount of salt remaining under abandoned pits was not significantly different from the produced waters after 10 years and could be a source of pollution for many decades. The leachate plumes were found to spread laterally and downward to the water table. Thus, there is a possible source area for continued brine contamination of the Pecos Alluvium with the city of Kermit as a receptor. Because of the preponderance of data, this area is possibly at significant risk and should be considered as the primary area for future field operations.

The 1979 kriged TDS map shows that the brine plume east of Wink moved south about 3 miles in 10 years, about 30 times faster than the estimated groundwater velocity. The error variance shows this area to have high statistical reliability. This movement is toward an area of considerable agricultural and irrigation activity located near the southern county line. Ashworth (8) showed that the Pecos Alluvium water table has been drawn down about 16 feet in northern Ward County by this activity. The movement of the groundwater toward this area has, perhaps, helped to protect the town of Wink by drawing the brine away from city water wells. Additional geologic data indicate the possibility of the plume passing under Wink due to the thickness and depth of the aquifer and the density contrast of oil field brine and fresh water. The area east of Wink is possibly at low risk compared to the area west of Kermit. Some field sampling may be considered to verify the present position and level of brine contamination in this area.

The 1979 map shows little or no brine contamination north and west of Wink compared to the high levels of brine shown on the 1957 map. The 1979 data shows a high error variance in this area due to a lack of data, thus making the 1979 data in this area suspect. Because this area is up-gradient from Wink, making Wink a possible receptor, this area should be considered as under a "possible risk" and field sampling may be needed to verify the level of any brine contamination in this area

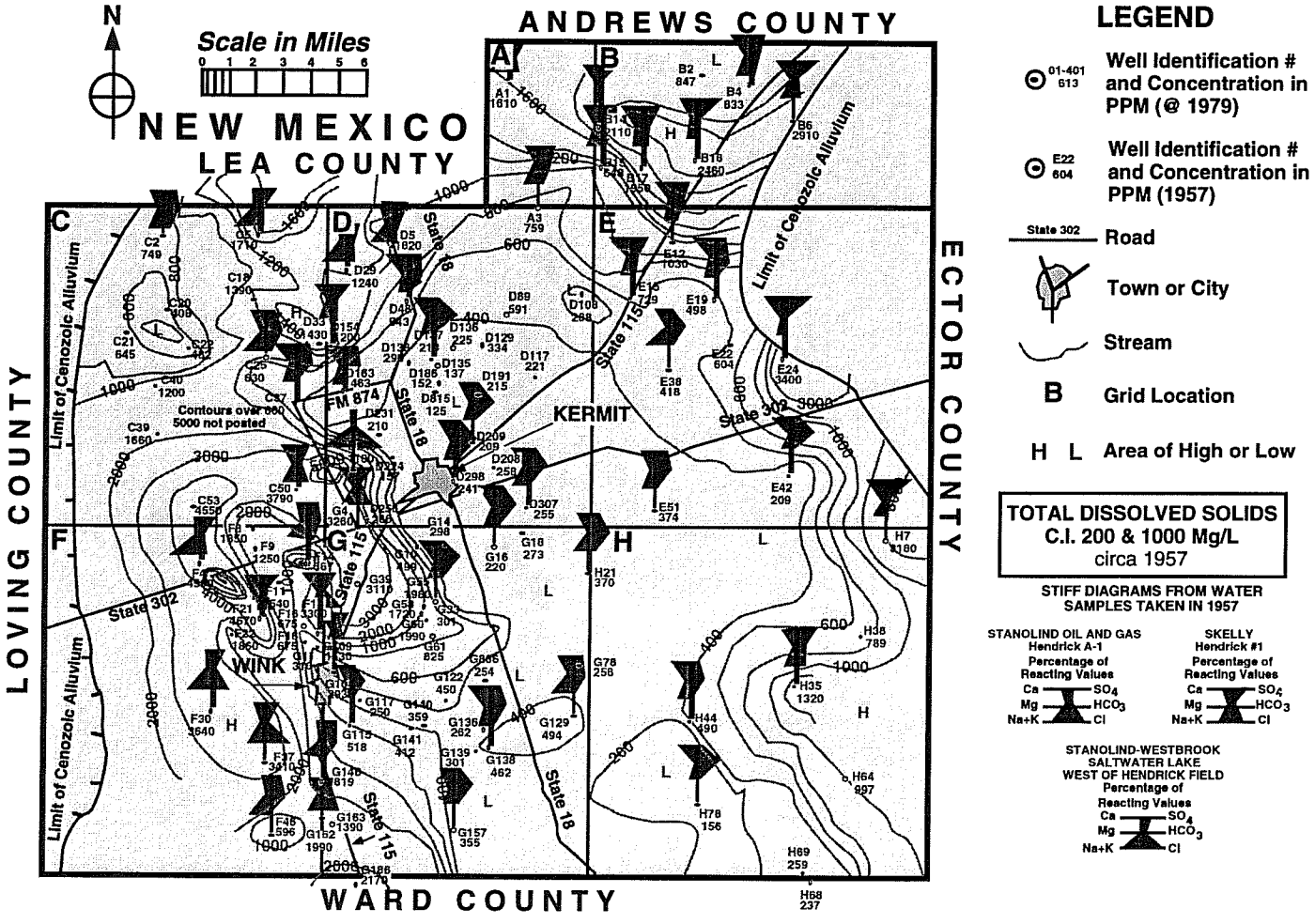


Figure 11. Kriged map of 1957 Winkler County, Texas, TDS concentrations with Stiff diagrams.

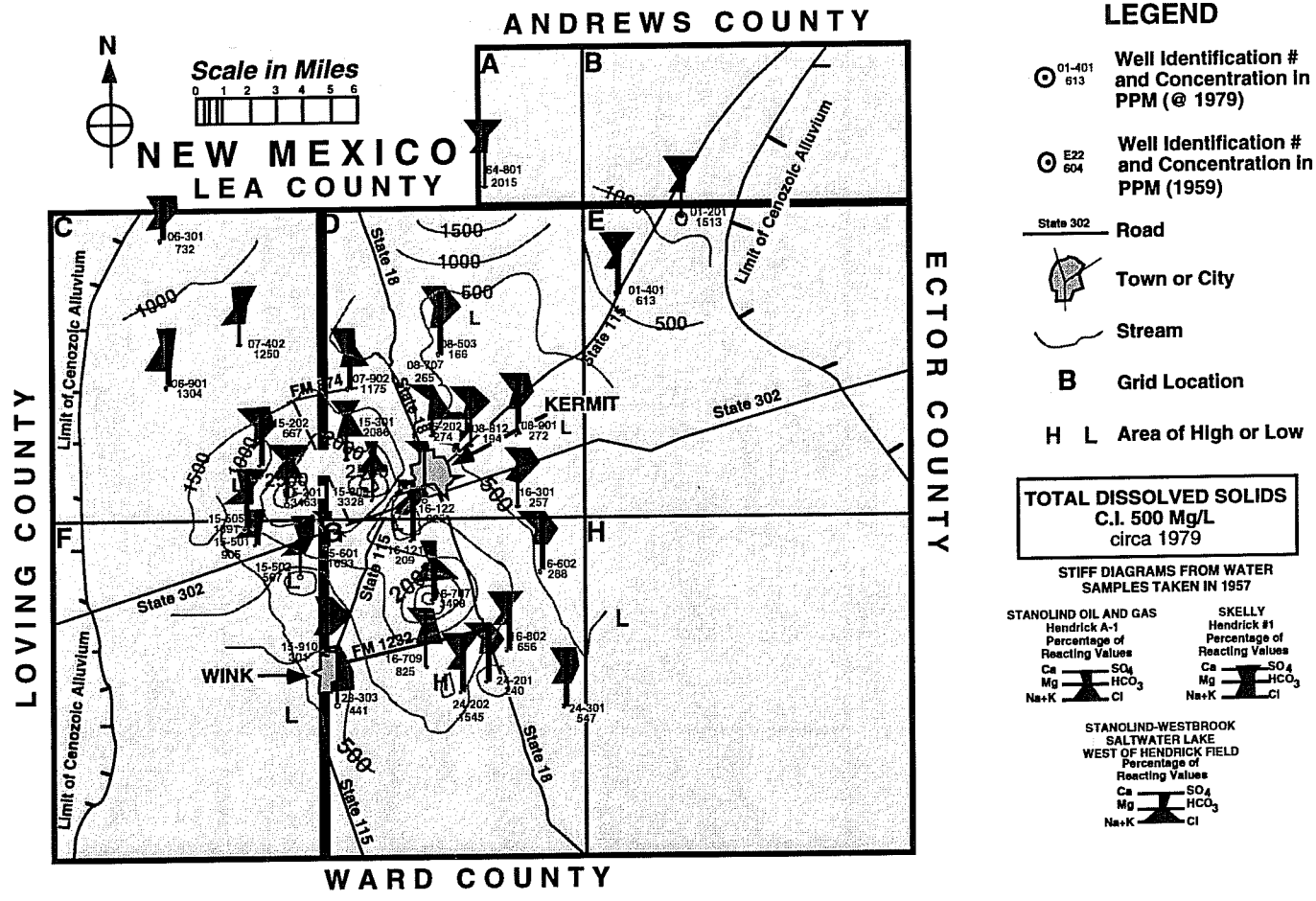


Figure 12. Kriged map of 1979 Winkler County, Texas, TDS concentrations with Stiff diagrams.

CONCLUSIONS

All data were acquired at minimal cost and in most cases were free. Public-domain geostatistical software was obtained from the U.S. Environmental Protection Agency and used on a 486-based PC to perform the variogram analysis and kriging. A 486 PC AutoCAD-based GIS was purchased as surplus from an engineering company for around $100. Historical aerial photography was purchased from the U.S. Department of Agriculture and the U.S. Geological Survey for reproduction costs and shipping. About one man-month of time was used to perform data acquisition and analysis, and final report preparation.

For a very small expenditure of time, materials, and personnel, a large area was evaluated for possible environmental risk, and three areas were located that may be at risk. An overview of the surface geology, hydrogeology, and history of the area was obtained. The geostatistical analysis helped to reduce the size of the area by creating unbiased maps and estimating the reliability of the data. This, in turn, established a focus for future field efforts that will lead to a reduction in field costs.

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Effects of Remediation on Soil Microfungi Following a Brine Spill in the Tallgrass Prairie

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ABSTRACT

Following a brine spill in March 1995 at the Tallgrass Prairie in Pawhuska, Oklahoma, several soil remediation treatments were employed. Approximately five months after the spill, a number of soil samples were collected from each treatment zone using sterile 50 ml tubes. Samples were stored under refrigeration until used. One gram of each sample was dilution plated in duplicate onto malt extract agar (MEA), malt extract agar plus 7% NaCl (MEA+NaCl), and dichloran glycerol agar (DG-18). All media contained streptomycin at a final concentration of 500 µg/ml. Plates were incubated at room temperature for 5 to 7 days for MEA and MEA+NaCl and 7 to 14 days for DG-18. Following incubation colonies were counted and identified to genus. The water content of each soil sample was determined and fungal concentrations were expressed as colony forming units per gram dry weight of soil (CFU/g). The highest mean concentrations of soil fungi were found in Treatment 3 (added sulfur, fertilizer, and hay); however, only samples from one site (6-6) in this treatment zone had significantly higher concentrations. Samples from Treatment 2 (added Salt Away II) had the greatest concentrations of salt tolerant fungi on the treated areas; however, samples collected from two areas on the fringe of the spill had the highest overall concentration of salt tolerant fungi. By contrast, the untreated zone in the spill area had the lowest concentration of salt tolerant species. Throughout the brine spill area, the most commonly identified fungi were species of *Aspergillus, Fusarium*, and *Penicillium*. In an area of the prairie not involved in the spill, the concentrations of these genera were somewhat lower than the study zone even though the overall concentrations of microfungi were not appreciably different.

INTRODUCTION

The tallgrass prairie once occupied a vast area in central North America covering about 3% of the continent (1). It was a complex ecosystem with a rich diversity of plant and animal life. Today, only a small portion of the original prairie remains, the rest having been converted to farm land. The largest remaining region of tallgrass prairie extends from northeast Kansas south into northeast Oklahoma (1).

In biomes such as the tallgrass prairie, the nutrient quality of the vegetation is generally low, and rainfall is limiting. As a result, dead plant material decomposes at slow rates. In the absence of fire or grazing animals, large amounts of litter accumulate (1). In these areas fungi often play a greater role in the decomposition process than bacteria (2). Over 80% of the decomposer biomass may be fungal biomass in grassland ecosystems (3). Saprobic fungi have a wide range of enzyme systems that are capable of decomposing most complex organic substrates such as proteins, cellulose, hemicellulose, and lignin. Since few fungi possess the complete set of enzymes necessary to totally decompose a substrate, a succession of fungal types typically colonize the substrates in the litter. This succession has only been studied in a limited number of ecosystems, and the species diversity of microfungi in most soil communities is unknown.

England and Rice (4) examined the occurrence of soil fungi over a 12 month period in two grassland plots in McClain County of central Oklahoma. One plot was located in a stand of tallgrass prairie, and the second was in abandoned farm land approximately 0.4 km away. They found that the mean concentration of fungi was always greater in the abandoned field. Concentrations in both plots were highest in the spring and lowest in the summer. A total of 136 species of fungi were identified from these plots with distinct differences between the sites. The abandoned field consistently had a greater number of species. Species of *Fusarium, Mucor, Penicillium, Trichoderma*, and *Aspergillus* were among the principal species isolated from the prairie plot with an occurrence of 20% or more.

The Tallgrass Prairie Preserve near Pawhuska, Oklahoma is one of the few remaining tracts of native tallgrass prairie in northeast Oklahoma. The Preserve spans more than 30,000 acres and is maintained by the Nature Conservancy. In early March 1995, a pipeline carrying brine ruptured at an injection well on the prairie spraying salt water over an area that was approximately 100 m x 100 m. The spill resulted in a complete loss of vegetation on the contaminated area. Several soil remediation treatments were employed shortly after the spill (Table 1). The present study was undertaken to examine the effects of the brine spill and these treatments on the population of soil microfungi.

METHODS

Approximately five months after the brine spill, a number of soil samples were collected using sterile 50 ml tubes. Each treatment zone was

sampled (Fig. 1) as well as untreated areas, areas on the fringe of the spill, and prairie sites far removed from the spill (not on map). Soil samples were sealed and stored under refrigeration until used.

One gram of each sample was dilution plated in duplicate onto malt extract agar (MEA), malt extract agar plus 7% NaCl (MEA+NaCl), and dichloran glycerol agar (DG-18). All media contained streptomycin at a final concentration of 500 μg/ml. MEA is an all purpose medium that is routinely used for culturing fungi. DG-18 selects for xerophilic fungi and is commonly used in cultivating fungi from foods and dust, while MEA+NaCl selects for salt tolerant fungi.

Plates were incubated at room temperature (25°C ± 2°C) for 5 to 7 days for MEA and MEA+NaCl and 7 to 14 days for DG-18. Following incubation fungal colonies were counted and identified to genus level using standard keys (5, 6, 7). The water content of each soil sample was determined by oven drying at 65°C for 24 hours, and fungal concentrations were expressed as colony forming units per gram dry weight of soil (CFU/g).

Soluble salts were extracted from dried soil samples using ultra-high purity water, and the extracts were analyzed using an atomic absorption spectrophotometer in either the atomic absorbance or atomic emission mode. Results were reported as wt. ppm sodium in dried soil (8).

RESULTS

Microfungi were isolated from all soil samples and on all media types. The highest mean concentration of all soil microfungi was found in Treatment 3 (Fig. 2). However, only samples from site 6-6 in this treatment zone had significantly higher concentrations. Soil samples on MEA and DG-18 media from site 6-6 in Treatment 3 were an order of magnitude greater than other sites, 6.95×10^5 CFU/g on MEA and 6.3×10^5 CFU/g on DG-18. The data from these cultures shows that *Chrysosporium* sp. at a concentration of 6.7×10^5 CFU/g on MEA was responsible for the high concentration from that site. However, on DG-18 there were 6.14×10^5 CFU/g of a non-sporulating fungus, possibly suggesting that this was a strain of *Chrysosporium* unable to sporulate on DG-18. The concentration of *Chrysosporium* on MEA+NaCl from this soil sample was 3.1×10^4 CFU/g, approximately 20 times lower than on MEA, suggesting that the presence of NaCl in the medium may have been inhibiting this isolate.

The highest concentrations of microfungi occurred on MEA but these were not significantly different than the concentrations on DG-18, $p>0.05$. In all areas, the concentrations of salt tolerant microfungi (able to grow on MEA with 7% NaCl) were lower than concentrations on non-salt media (Fig. 2); however, the means on MEA+NaCl were not significantly different than those on other media ($p>0.05$). Although the sodium concentrations within the study site were highly variable (Table 2), overall the concentration of salt tolerant fungi showed a statistically significant correlation to the soil sodium concentration (Fig. 3, $r^2=0.36$; $p<0.01$). When samples from the four remediated areas were compared, samples from Treatment 2 had the greatest concentrations of salt tolerant fungi (Fig. 4). However, samples collected from two areas on the fringe

of the spill had the highest overall concentration of salt tolerant species. By contrast, the untreated zone in the spill area had the lowest concentrations of salt tolerant species.

Throughout the spill area, the most commonly identified fungi on all media were species of *Aspergillus*, *Fusarium*, and *Penicillium* (Table 3). For these three genera, multiple species were isolated although identification to species level was not consistently carried out. In soil samples from the prairie area, not involved in the spill, the concentrations of these three genera were somewhat lower than in the study zone even though the overall concentrations of microfungi were not appreciably different.

DISCUSSION

Microfungi were isolated from all prairie areas sampled. Mean concentrations in soil samples from the brine spill area were not appreciably different than those from the unaffected area of the prairie. In fact, the concentrations from many samples in the spill were higher than the uncontaminated area. Because there were no soil samples collected at the time of the spill, it is difficult to know the immediate effects of the brine spill on the fungi. It is also not possible to determine the impact of the nutrient influx following the death of the vegetation or the effect of the remediation process itself and the rate of recovery of the population of microfungi.

The concentrations of soil microfungi reported here are within the ranges of soil fungi from other studies (9); however, the concentrations are somewhat higher than those found in the previous study of Oklahoma prairie soils. England and Rice (4) found that the highest mean concentration of soil fungi from a tallgrass prairie plot occurred in May with $1.7x10^4$ fungi per gram of soil. In the present study the concentrations ranged from $4.0x10^3$ CFU/g to $6.9x10^5$ with the mean concentration on MEA and DG-18 at $9.9x10^4$ CFU/g and the mean on MEA+NaCl at $4.7x10^4$. England and Rice (4) reported that the lowest concentrations occurred in the summer. Although they collected no samples in August, the means for July and September were $3.8x10^3$ and $2.8x10^3$ fungi/g, respectively. The higher concentrations reported in the present study may be due to differences in methodology since England and Rice (4) used direct soil plating rather than dilution plating. It should be noted, that if the tallgrass prairie soils typically have the lowest concentrations of soil microfungi in summer as reported by England and Rice (4), then the concentrations found in the present study could actually represent the minimum annual level of soil fungi.

The principal genera isolated at this site were *Penicillium*, *Aspergillus*, and *Fusarium*. Several species of each genus were found in the brine spill area. These results are similar to those from noncontaminated grassland areas (10) including sites in Oklahoma (4). In addition, the salt tolerance of several *Aspergillus* and *Penicillium* species is well known (11). Little is known about the salt tolerance of *Fusarium* species; however, the ability of *Fusarium* species to grow on substrates with low water potential has been studied (12).

A major problem encountered in saline soils is obtaining water from a soil with a negative water potential. At low water potentials bacterial activity in the soil decreases, and in areas where the soil water potential is below -2 MPa, respiration in the soil is due entirely to fungal activity (2, 11). At very low water potentials, below -15 MPa, xerophilic species of *Aspergillus* and *Penicillium* dominate the community of soil microfungi (11).

Certain species of fungi are remarkable in their ability to tolerate high salinities. Cultures of *Basipetospora halophilia, Exophiala werneckii*, and *Aspergillus penicilloides* isolated from salted, dried fish were able to grow on NaCl-saturated media (11). These species exhibited growth optima at salinities corresponding to 2.5 M NaCl (-15 MPa). Overall, fungi are able to tolerate a range of water potentials between -5 and -69 MPa (12). The salt concentration (-7 MPa) used in the MEA+NaCl medium in the present study is well within this range. In addition, the sodium concentrations measured in the soil samples (five months following the spill) are also well within the general range tolerated by fungi.

The capacity of many soil fungi to adapt to high concentration of NaCl in the soil is an advantage for the restoration of salt-contaminated soils. The restablishment of microfungi will permit the return of the saprobic activity to the area. This is especially important in grassland biomes where microfungi are the major components of the decomposer biomass (3).

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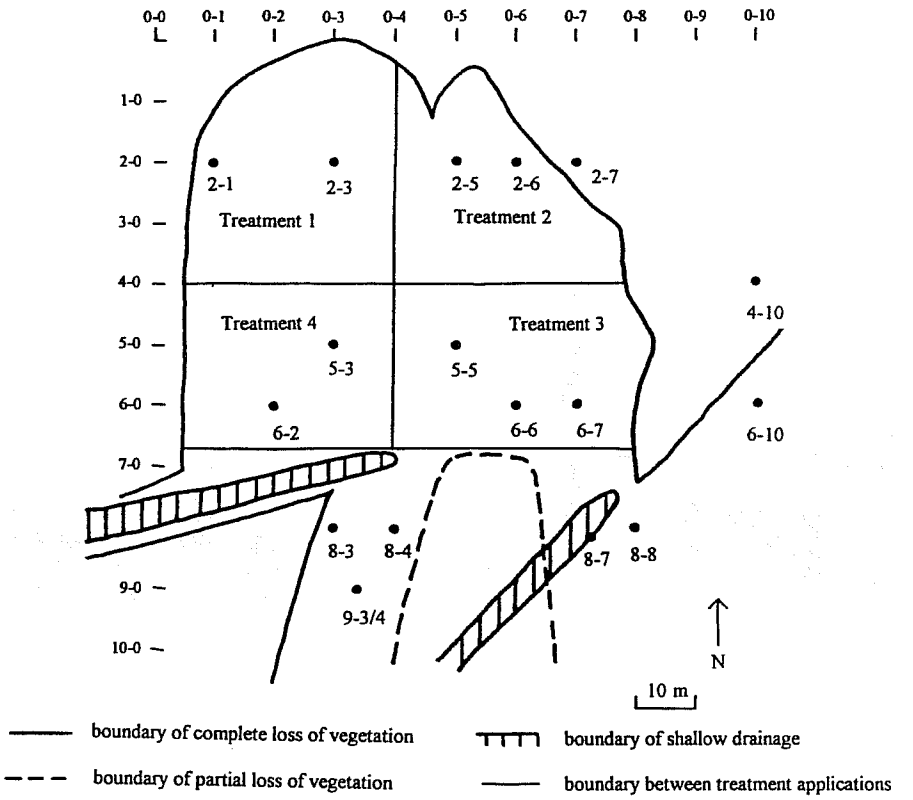

Figure 1. Location Map of Soil Samples

Table 1

Soil Remediation Treatments Used on a Brine Spill at the Tallgrass Prairie Preserve

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Treatment 1 -- Area ripped with dozer*, sprayed with Salt Away II (27.5 gal in 30 barrels water), sprayed with Adsee 799 (5 gal in 6.6 barrels water).

Treatment 2 -- Area ripped with dozer*, sprayed with Salt Away II (27.5 gal in 30 barrels water).

Treatment 3 -- Spread with 300 lb sulfur, spread 25 lb 10-20-10-7 pelleted ammonium phosphate fertilizer, ripper with dozer*, spread 65 seed hay bales, hay tracked down with dozer, soaked with 38 barrels water.

Treatment 4 -- Ripped with dozer*, Sprayed with Adsee 799 (10 gal in 13.3 barrels water).

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* All dozer ripping consisted of 12-14" deep furrows on 18" centers with contour

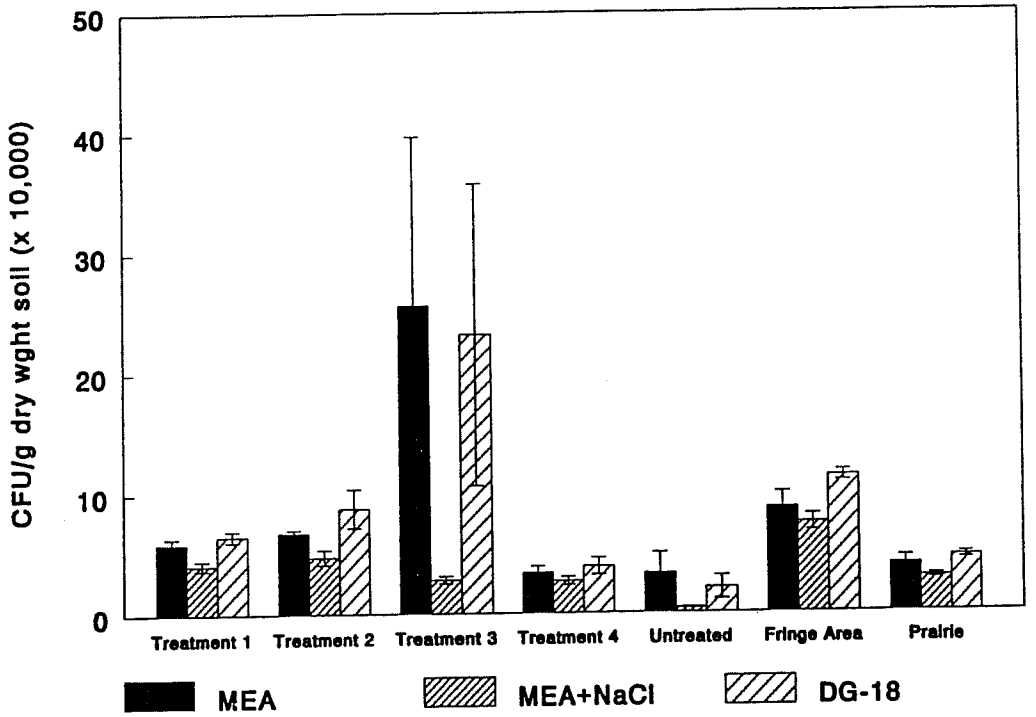

Figure 2. Concentration of Soil Microfungi Following Remediation of a Salt Spill

Table 2

Sodium Concentration of Soil Samples

Treatment	Soil Sample	Na^+ Concentration (ppm)
Treatment 1	2-1	6200
	2-3	2100
Treatment 2	2-5	2400
	2-6	2700
Treatment 3	5-5	5200
	6-6	2000
	6-7	950
Treatment 4	5-3	1400
	6-2	2100
No Treatment	8-3	1800
	8-4	2900
	8-7	380
	8-8	n.a.
	9-3/4	n.a.
Fringe Area	2-7	9500
	4-10	n.a.
	6-10	n.a.
Prairie	A	n.a.
	B	n.a.

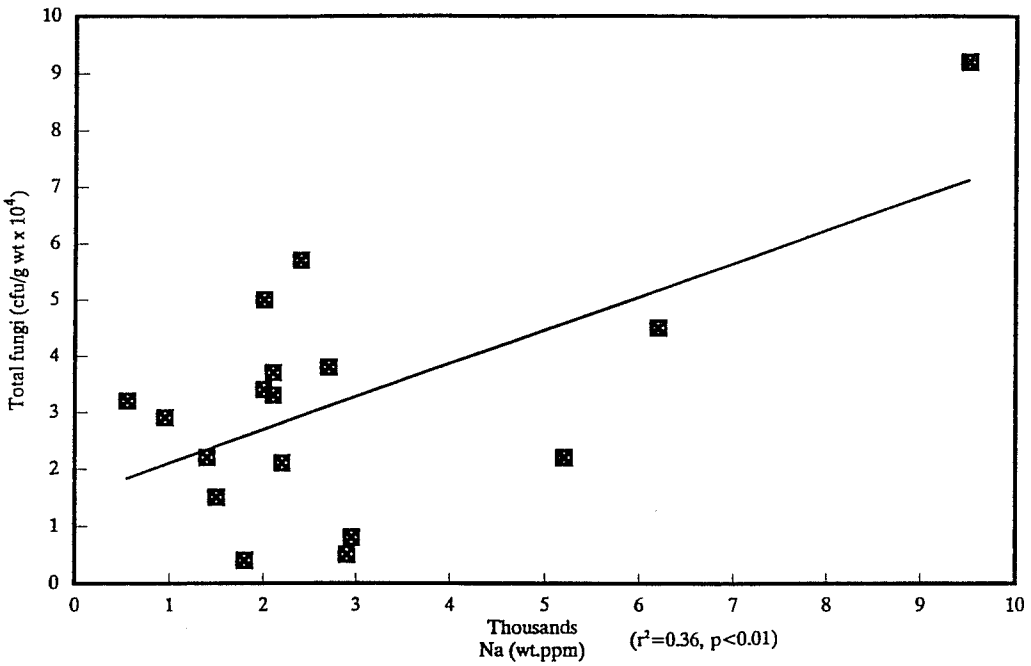

Figure 3. Correlation of Salt Tolerant Fungi with Soil Sodium Concentrations

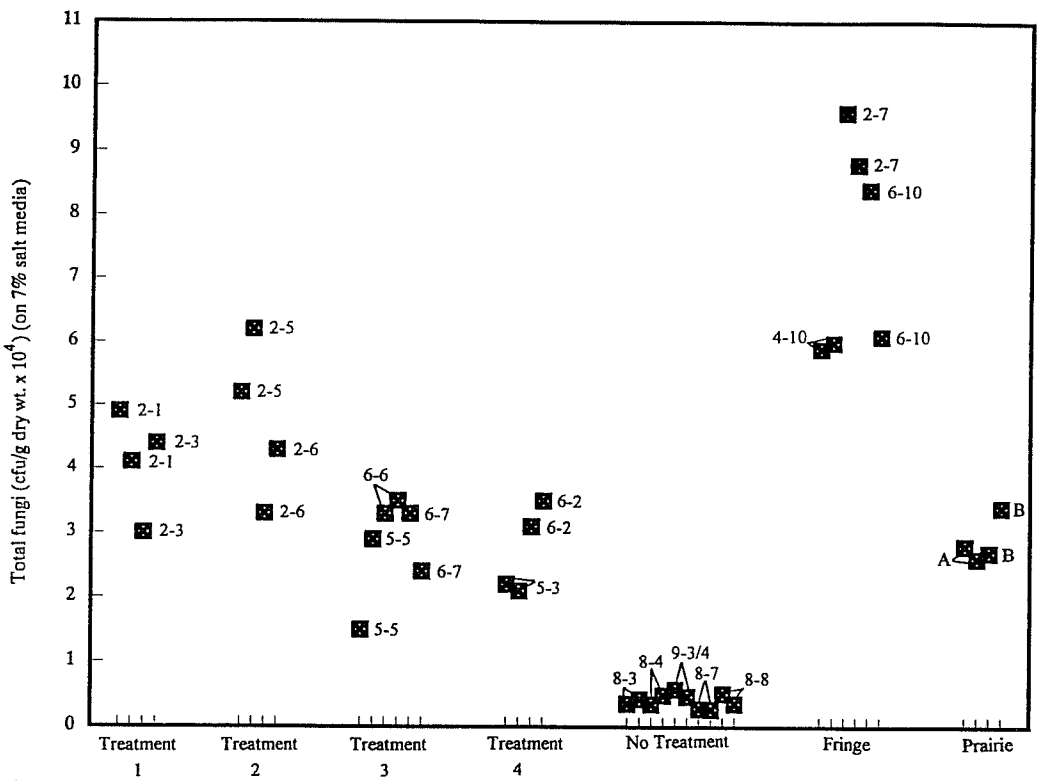

Figure 4. Effect of Soil Remediation on the Concentration of Salt Tolerant Fungi

Table 3

Mean Concentration of Salt Tolerant Fungi on Malt Extract Agar + 7%NaCl

Treatment	Concentration of Fungi in CFU/g Dry Weight of Soil			
	Aspergillus	*Fusarium*	*Penicillium*	All Others*
Treatment 1	0.6×10^4	1.5×10^4	0.2×10^4	1.9×10^4
Treatment 2	0.7×10^4	1.5×10^4	0.6×10^4	2.1×10^4
Treatment 3	1.1×10^4	0.2×10^4	1.3×10^4	0.8×10^4
Treatment 4	0.2×10^4	0.6×10^4	0.4×10^4	1.7×10^4
No Treatment	0.2×10^4	0.02×10^4	0.2×10^4	0.5×10^4
Fringe Area	2.3×10^4	0.2×10^4	0.3×10^4	5.3×10^4**
Prairie	0.4×10^4	0.3×10^4	0.4×10^4	1.3×10^4

* All others refers to genera other than *Aspergillus*, *Fusarium*, and *Penicillium* as well as non-sporulating fungi.

** *Chrysosporium* sp had a mean concentration of 2.4×10^4 in this area but was only identified in sample 2-7 where the concentration was 7.2×10^4.

Transport of Brine Contamination from a Recent Produced Water Spill

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The Nature Conservancy

ABSTRACT

Oil field operations typically impact the environment through various spills. In March 1995, a steel pipe transporting brine to an injection well ruptured resulting in contamination of a 1 to 2 acre site in the Tallgrass Prairie Preserve. Loss of vegetation quickly resulted. Spontaneous revegetation of the site is unlikely due to the toxicity of the brine to plant life and erosion of top soil which will result from the original loss of vegetation.

This brine impacted site has been intensely sampled twice in sampling events 11 months apart. Over the 11-month period, sodium and electrical conductivity in soil samples taken from the contaminated site decreased while water samples from a downslope drainage receiver showed an increase in both sodium and electrical conductivity. Sodium and electrical conductivity of soil samples from a intermediate drainage trough also appear to have increased over the same period. This preliminary study has shown that brine components rapidly migrate away from the original site of contamination. The impact of these brine components on soil and surface water receptors downgradient of the spill is currently under investigation.

* corresponding author

INTRODUCTION

The Tallgrass Prairie once spanned approximately 142 million acres over 14 states in an area currently known as the "Bread Basket". Today, less than 10% of the original prairie ecosystem remains. The only large tracts are located in the Flint Hills of Kansas and Oklahoma. Smaller plots of a few acres can be encountered throughout the midwest.

In 1989, The Tallgrass Prairie Preserve was created when The Nature Conservancy purchased 30,000 acres of the Chapman-Barnard Ranch. Since the initial purchase, an additional 6,000 acres of Osage County prairie land has been added. The preserve is located approximately 17 miles NW of Pawhuska, OK and lies inside the Osage oil fields which have been exploited since the beginning of this century. The mineral rights are owned by the Osage Nation.

Historically, oil field operations in Osage County, OK have resulted in environmental damage from produced water spills. In the past, remediation or clean-up may or may not have been attempted. The usual remedy was for the responsible party to pay the land owner a cash disbursement associated with the loss of use of the land for a set period of years. Prairie land, not including any mineral rights, has little remunerative value aside from grazing or farming.

The Nature Conservancy desires to restore damaged sites in the Preserve in keeping with its goals of restoring the native prairie ecosystem. In this regard, The Nature Conservancy works closely with the independent producers and the Osage Nation to minimize the impact of current production activity. Remedial actions for any environmental problems associated with oil field operations in the Preserve must be low in cost since resources are limited. The University of Tulsa and The Nature Conservancy are working together in the Preserve to restore damaged sites and train tomorrow's environmental engineers and environmental scientists, jointly serving the goals of both institutions. This study is a result of that collaboration.

The purpose of the work described here has been to study the migration of brine components downgradient of a recent produced water spill. The time course of events following a brine contamination is important to understanding the ultimate impact of these spills. The economic value of all resources (land, surface water, and groundwater) ultimately impacted by these events is the proper measure of the economic impact of the spill as opposed to the value of the land immediately

impacted. This is an ongoing study; therefore, this paper represents a preliminary study.

In March 1995, a steel pipe transporting brine to an injection well split. Figure 1 shows the position of the resulting brine spill (Site C) relative to the remainder of the overall Preserve study area. The area impacted by the spill (100 meters by 100 meters with a 1 meter per 50 meter downslope) was originally covered with native prairie grasses at the time of the incident. The soil was depicted as a combination Steedman and Coweta series which was appropriate for the native grasses which were present. These grasses are intolerant of brine contamination and the area quickly became denuded of all vegetation after the event. Topsoil, which can be very thin throughout this region of the prairie, quickly erodes after vegetation loss (1).

SAMPLE GATHERING AND ANALYSIS

Soil Samples

Soil samples were collected from the surface of the contaminated site during August 1995 and June 1996. Sample location for the contamination zone was determined via land grid referenced to the brine injection well. The land grid was produced using a 100 meter tape and a surveyors transit. Sample spacing for the August, 1995 sampling was at 10-meter intervals while sample spacing for the June 1996 sampling was at 20-meter intervals. Sample location for the drainage trough was determined via stepped off distance referenced to the contamination zone. For each sample, approximately 250 grams of soil was placed into a one pint plastic bag which used a plastic zipper for closure. Immediately after collection, the samples were placed into a Styrofoam icebox for cold storage (1).

The soil samples from the contamination zone represent a combination of the geologic Zone A & B subsurface horizon. The A Zone is generally considered to be the zone of leaching and is characterized by the downward movement of water. For the contaminated area, the A Zone is represented by the first 4 to 8 inches of soil (Steedman and Coweta series). Prior to the contamination, the A Zone soil was classified as having a low shrink/swell potential with an available water content of approximately 0.15 inches of water per inch of soil. The B Zone is generally considered to be the zone of accumulation and is characterized by the accumulation of material leached downward from the A Zone. For the contaminated area, the B Zone is represented by the incremental depth to approximately 30 inches. Prior to the contamination, the B Zone soil

was classfied as having a high shrink/swell potential for the Steedman part and a low shrink/swell potential for the Coweta part with an available water content of approximately 0.12 inches of water per inch of soil (2,3).

Soluble salts were extracted from the soil samples as follows. A 150-g mass of the soil was dried on a glass plate in a convection oven at 55 °C for a minimum of 24 hours. The resulting sample was ground and sieved through a metal sieve plate which was sufficiently fine to remove 1-mm diameter rocks. Precisely 100.0 g of the sieved soil was thoroughly mixed with 100.0 mL of ultra-high purity water in a 150 mL Pyrex beaker using a glass stirring rod. The resulting soil/water mixture was filtered using a Buchner funnel and Whatman #1 filter paper under vacuum.

The soil extract was analyzed for sodium using a Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer (589 nm and 0.7 slitwidth). The samples which were collected during August 1995 were analyzed using the atomic absorption mode whereas the atomic emissions mode was used for samples collected during June 1996. A 1.00 wt. ppm sodium standard solution produced a single point calibration curve which was well within the linear region for absorbance versus concentration for the atomic absorption analyses. The atomic emissions analyses allowed use of a second order non-linear calibration curve using 20, 30, and 40 wt. ppm sodium standard solutions. Dilutions of each extract were necessary to obtain the applicable absorbance range for analysis. The sample results for sodium are given in wt. ppm sodium in dried soil and corrected for dilution of the extract.

Electrical conductivity was determined using a YSI Model 31 electrical conductivity bridge and a Cole Parmer electrical conductivity cell. Approximately 40 mL of extract was required for this analysis. A 100-mL glass graduated cylinder was used as the cell and sample holder.

Water Samples

Water samples were collected from the drainage receiver (Pond 18) throughout the period from August 1995 to September 1996. A minimum of 500 mL was obtained at each sampling in LDPE or HDPE bottles. These samples were analyzed for sodium and electrical conductivity using the equipment previously described.

DATA GATHERING AND ANALYSIS

Land grid data were obtained from Whitestar (Englewood, Colorado). The well head location data were obtained from Petroleum Institute and NRIS-University of Oklahoma (Norman, Oklahoma). The topography and stream data were obtained from USGS (EROS Data Center, Sioux Falls, South Dakota). All were obtained in electronic form.

The analytical results were transcribed into a spreadsheet {PC computer environment}. The land grid data, wellhead locations, topography and analytical results were merged into ARCVIEW software {UNIX computer environment} to produce maps (Figures 1, 2, 3, 4, and 5) for further analysis.

The maps produced using ARCVIEW software show the well head locations, topography, stream, and sample locations. The sample locations are shown in shades of gray according to intensity of contamination for the soil samples (contamination zone and the drainage trough) and also for the liquid samples (Pond 18). The well head locations are shown for past and present well heads, whether or not a pumping unit or other unit is in place or active at this time.

RESULTS

A comparison of the maps (Figures 2, 3, 4, and 5) from August 1995 and June 1996 shows that sodium and electrical conductivity decreased in the contaminated site soil over this eleven month period. The concentration of highly contaminated samples is greater for August 1995 than June 1996. Additionally, relatively low contamination levels are evident in the upslope portion of the contaminated site in the June 1996 maps (Figures 3 and 5). No uncontaminated samples were revealed in the August 1995 maps (Figures 2 and 4).

During the sampling of August 1995 and also the sampling of June 1996, the soil samples obtained from the drainage trough showed higher than background levels of sodium and electrical conductivity. However, the intensity of contamination appears to have increased over the eleven month period. During the same period, both sodium and electrical conductivity increased in the downstream drainage receiver (Pond 18).

After the spill during March 1995, the land became quickly denuded of vegetation. Vegetation has not been re-established in the contaminated site since the spill.

CONCLUSIONS

These data show that brine components rapidly migrated away from the original site of contamination. The impact of these brine components on soil and surface water receptors downgradient of the spill is currently under investigation.

ACKNOWLEDGEMENT

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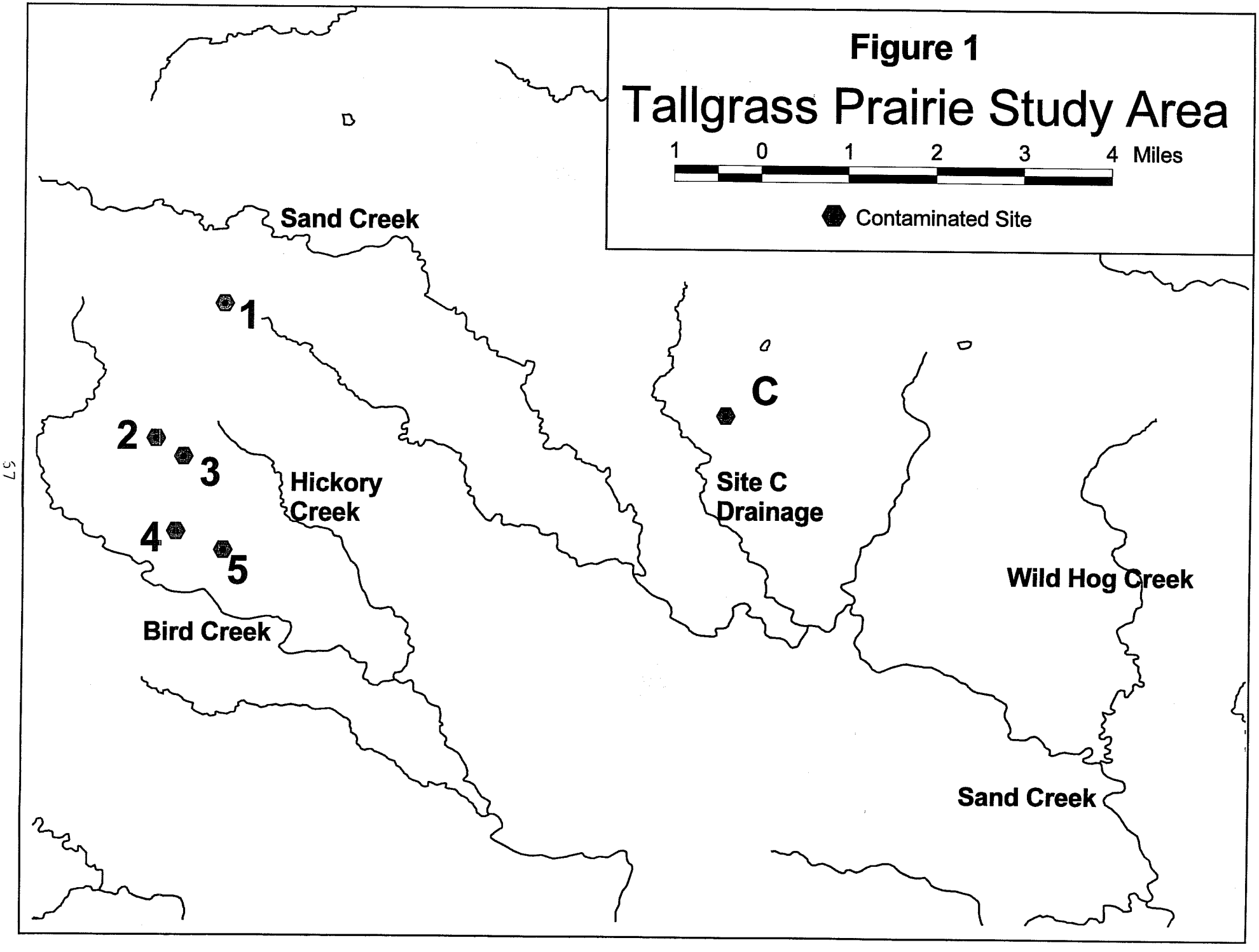


Figure 1
Tallgrass Prairie Study Area
1 0 1 2 3 4 Miles
Contaminated Site
Sand Creek
1
C
2
3
Hickory Creek
Site C Drainage
4
5
Wild Hog Creek
Bird Creek
Sand Creek

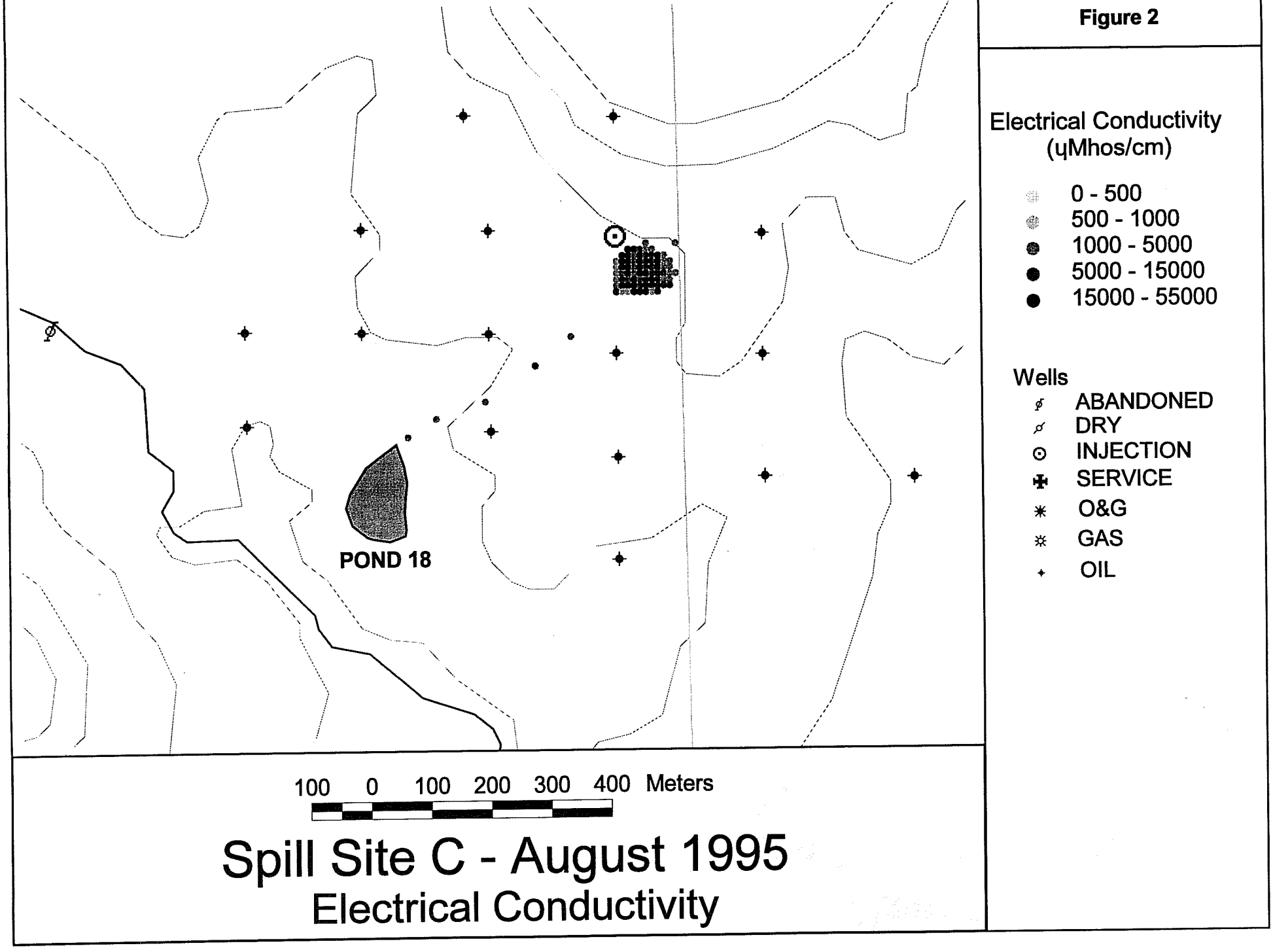


Figure 2
Electrical Conductivity (µMhos/cm)
0 - 500
500 - 1000
1000 - 5000
5000 - 15000
15000 - 55000
Wells
ABANDONED
DRY
INJECTION
SERVICE
O&G
GAS
OIL
POND 18
100 0 100 200 300 400 Meters
Spill Site C - August 1995
Electrical Conductivity

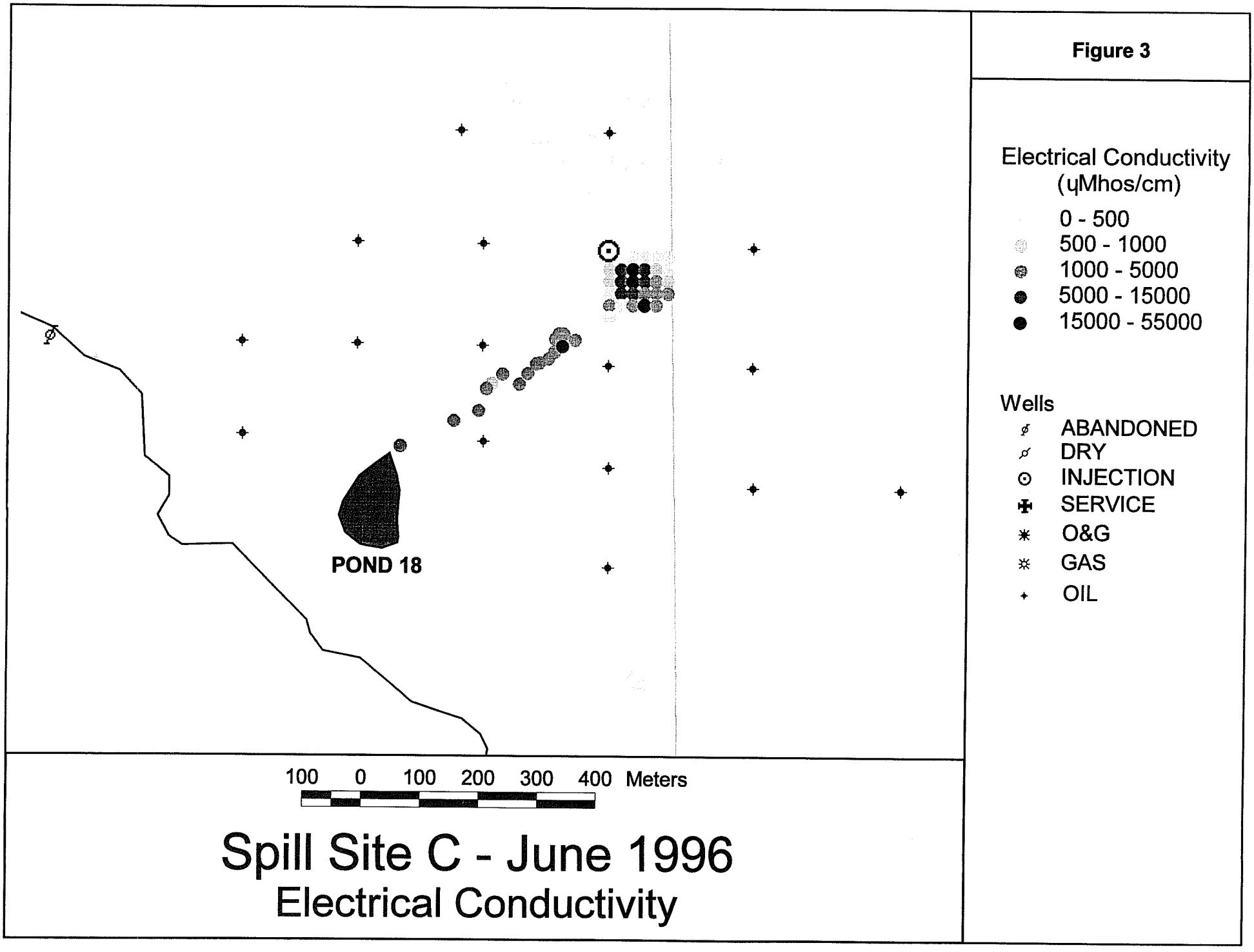
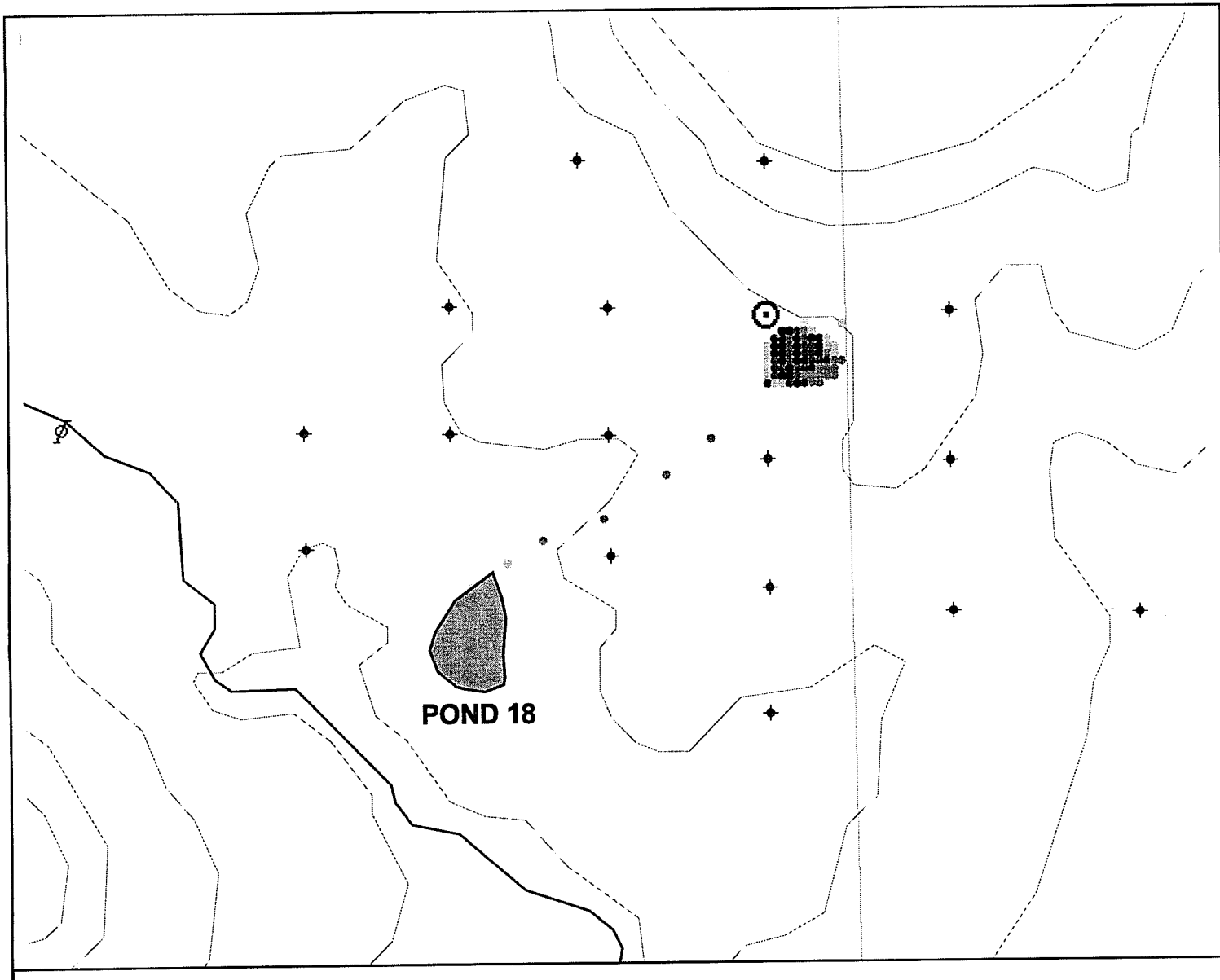


Figure 3
Electrical Conductivity
(µMhos/cm)
0 - 500
500 - 1000
1000 - 5000
5000 - 15000
15000 - 55000
Wells
ABANDONED
DRY
INJECTION
SERVICE
O&G
GAS
OIL
POND 18
100 0 100 200 300 400 Meters
Spill Site C - June 1996
Electrical Conductivity

Figure 4



Na (wt. ppm)
- 0 - 25
- 25 - 250
- 250 - 1000
- 1000 - 2500
- 2500 - 10000

Wells
- ABANDONED
- DRY
- INJECTION
- SERVICE
- O&G
- GAS
- OIL

100 0 100 200 300 400 Meters

Spill Site C - August 1995
Sodium

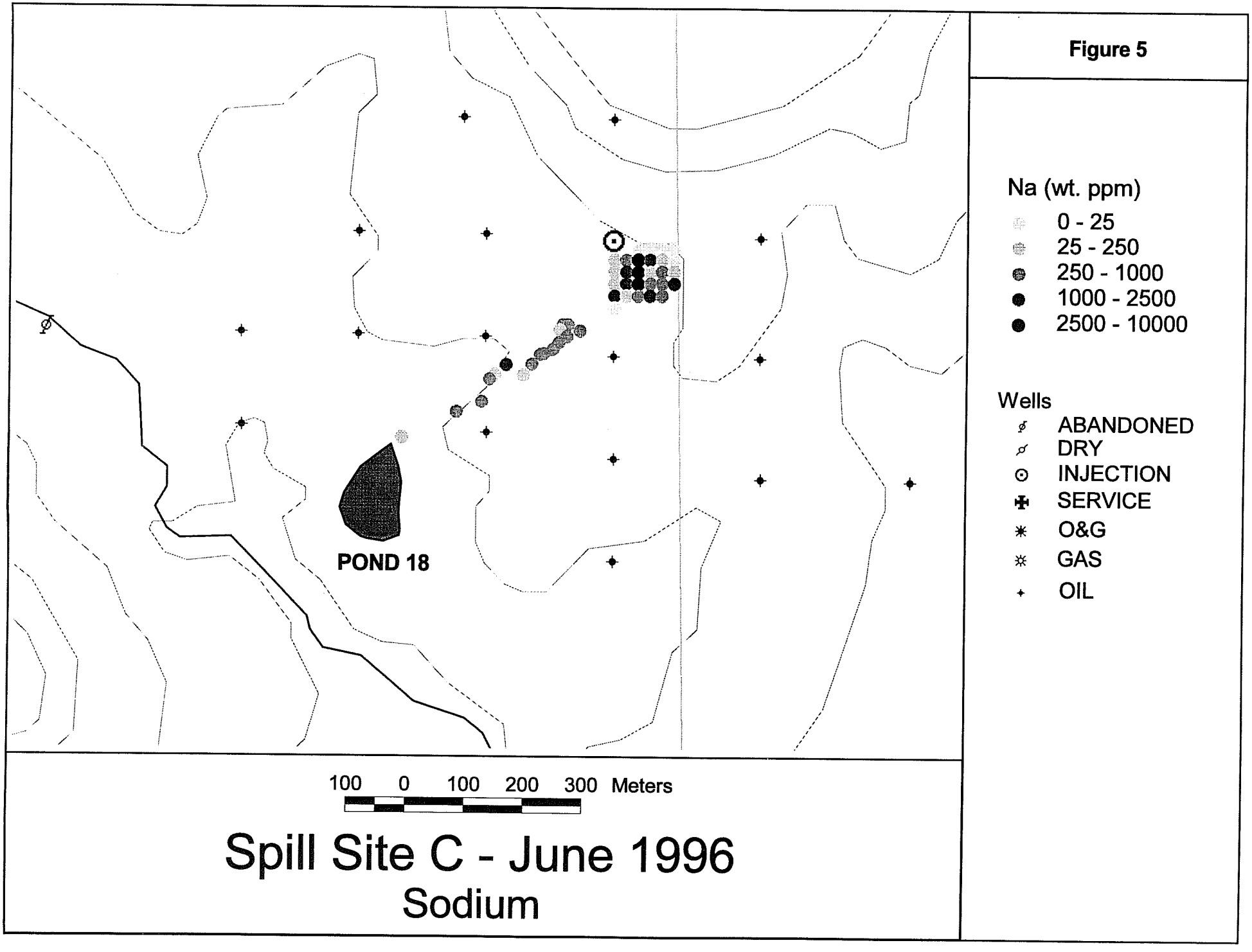


Figure 5
Na (wt. ppm)
0 - 25
25 - 250
250 - 1000
1000 - 2500
2500 - 10000
Wells
ABANDONED
DRY
INJECTION
SERVICE
O&G
GAS
OIL
POND 18
100 0 100 200 300 Meters
Spill Site C - June 1996
Sodium

Correlation of Surface Water Quality and Oil Production

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The University of Tulsa

R. Hamilton
The Nature Conservancy

ABSTRACT

The Tallgrass Prairie Preserve in Osage County, OK contains over 120 producing oil wells and five historic brine scars. These past and current production activities represent potential sources of brine contamination in the surface waters of the Preserve. A survey has been initiated to determine the extent of brine contamination in the ponds and creek systems in the Preserve. The goal of this survey is to ultimately determine the relationship of this contamination to current activity and historic spills of produced water and determine the pathways for brine mobility in the Preserve. Initial results are presented.

* corresponding author

INTRODUCTION

The Tallgrass Prairie once spanned approximately 142 million acres over 14 states in an area currently known as the "Bread Basket". Today, less than 10% of the original prairie ecosystem remains. The only large tracts are located in the Flint Hills of Kansas and Oklahoma. Smaller plots of a few acres can be encountered throughout the midwest.

In 1989, The Tallgrass Prairie Preserve was created when The Nature Conservancy purchased 30,000 acres of the Chapman-Barnard Ranch. Since the initial purchase, an additional 6,000 acres of Osage prairie land has been added. The preserve is located approximately 17 miles NW of Pawhuska, OK and lies inside the Osage oil fields which have been exploited since the beginning of this century. The mineral rights are owned by the Osage Nation.

Historically, oil field operations in Osage County, OK have resulted in environmental damage from produced water spills. In the past, remediation or clean-up may or may not have been attempted. The usual remedy was for the responsible party to pay the land owner a cash disbursement associated with the loss of use of the land for a set period of years. Prairie land, not including any mineral rights, has little remunerative value aside from grazing or farming.

The Nature Conservancy desires to restore damaged sites in the Preserve in keeping with its goals of restoring the native prairie ecosystem. In this regard, The Nature Conservancy works closely with the independent producers and the Osage Nation to minimize the impact of current production activity. Remedial actions for any environmental problems associated with oil-field operations in the Preserve must be low in cost since resources are limited. The University of Tulsa and The Nature Conservancy are working together in the Preserve to restore damaged sites and train tomorrow's environmental engineers and environmental scientists, jointly serving the goals of both institutions. This study is a result of that collaboration.

In addition to over 120 producing oil wells, the Preserve contains five historic brine scars. Past and current production activity both represent potential sources of brine contamination in the Preserve. The purpose of this study was to make an initial survey of brine contamination in surface waters in the Preserve and determine the relationship of this contamination to current activity and historic spills of produced water. This is an ongoing study; therefore, this paper represents a preliminary report.

STUDY AREA

The study area (Figure 1) for this investigation lies within the Osage oil fields and includes approximately 40,000 acres containing five small land tracts known to have been heavily impacted by past brine contamination (brine scars). These historic brine scars are designated as sites 1, 2, 3, 4, and 5 (Figure 1). All of these tracts are within the land area purchased by The Nature Conservancy except for a portion of one contaminated site (Site #5) which lies outside the Preserve. The oldest sites are believed to be more than 50 years old. The most recent incident producing a contaminated site (Site C) occurred during March 1995 when a steel pipe which was transporting brine to an injection well split.

Several creek systems exist within the area of study. Sand Creek (Figures 6, 7A, and 7B) is the longest creek system within the study area and stretches diagonally northwest to southeast as shown on the maps. Sand Creek differs from the other affected creek systems in three ways: (1) there is no known incident of any major brine spill in the lands draining directly into Sand Creek, (2) in the upslope sector to the north and northwest, an oil field lies in very close proximity to Sand Creek, and (3) Sand Creek is not protected from oil-field drainage by topography. In the southern portion of the study area, Sand Creek receives waters from the Bird Creek System and the Site C drainage area and the Wild Hog Creek system. The Bird Creek system receives drainage from properties located outside the study area as well as Hickory Creek and Sites 4 and 5. Hickory Creek receives drainage from Sites 2 and 3. The Site C drainage would appear to be protected by geology from an oilfield to the east. Wild Hog Creek seems to be relatively uncontaminated from brine spills and scars (no physical evidence is visible).

SAMPLING AND ANALYSIS

Water samples (274) were collected from streams, creeks, ponds, water holes, and water puddles throughout the Preserve from August, 1995 to September, 1996. The location for each sample was obtained via an Eagle Accusport GPS. Location accuracy is valid to within 100 meters since the samples were obtained prior to elimination of the DOD inspired "wobble factor". A minimum of 500 mL was obtained at each sampling in LDPE or HDPE bottles. These samples were analyzed for sodium, chloride, and electrical conductivity after settling.(1)

Sodium analyses were accomplished using a Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer in either the atomic absorption or atomic emission mode. For the atomic absorption mode, a 1.00 wt. ppm sodium standard solution produced a single point calibration curve which was well within the linear region for absorbance vs. concentration. The atomic emission analyses allowed use of a second-order nonlinear calibration curve using 20, 30, and 40 wt. ppm sodium standard solutions. Dilutions of each sample were necessary to obtain the applicable absorbance range for analysis. The analytical results for sodium are given as wt. ppm sodium and are corrected for dilution of the original sample.

A Dionex Model DX-100 Ion Chromatograph with AS-40 Automated Sampler was employed for chloride analyses. The standard solution was produced by Dionex and contained fluoride (20 wt. ppm), chloride (30 wt. ppm), nitrate (100 wt. ppm), phosphate (150 wt. ppm), and sulfate (150 wt. ppm). The standard solution was diluted 1:49, 1:24, and 1:9 with ultra high purity water to provide the three necessary calibration solutions. Dionex ion chromatograph 5 mL plastic vials and caps were used as sample containers. The caps contained a filter to prevent contamination of the instrument. The samples were diluted as appropriate to obtain the proper range (< 3 wt. ppm chloride) for analysis. The analytical results for chloride are given in wt. ppm chloride and are corrected for dilution of the original sample.

Electrical conductivity was determined using a YSI Model 31 electrical conductivity bridge and a Cole Parmer electrical conductivity cell. Approximately 40 mL of water was required for each analysis. A 100-mL glass graduated cylinder was used as the cell and sample holder.

DATA GATHERING AND ANALYSIS

Land grid data were obtained from Whitestar (Englewood, Colorado). Well head location data were obtained from Petroleum Institute and NRIS-University of Oklahoma (Norman, Oklahoma). The topography and stream data were obtained from USGS (EROS Data Center, Sioux Falls, South Dakota). All data were obtained in electronic form.

The analytical results were transcribed into a spreadsheet {PC computer environment}. The land grid data, well location data, topography data, stream data, and also the analytical results were merged into ARCVIEW software {UNIX computer environment} to produce the enclosed maps (Figures 1, 2, 3, 4, 5, 6, 7A, and 7B) for further analysis.

The maps produced using ARCVIEW software show the well head locations, topography, stream, and sample locations. The sample locations are shown in shades of gray according to intensity of contamination. The well head locations are shown for past and present well heads, whether or not a pumping unit or other unit is in place or active at this time.

RESULTS

B Creek & Site C Drainage

As previously noted, Bird Creek receives drainage from the oldest contaminated land site (Site #5) and the Site C drainage system receives drainage from the newest contaminated land site (Site C). The maps (Figures 2, 3, 4, and 5) show, for both Bird Creek and the Site C drainage, sodium, chloride, and electrical conductivity are elevated relatively near the contaminated site. Contamination levels remain elevated and gradually decrease with distance from the site. However, the contamination levels do not decrease to background levels (shown by ponds which are not contaminated) within the area of study. Further evidence for the transport of sodium contamination from Site C to the downstream drainage receiver at the head of Site C drainage are provided by Yates et al (2).

Prairie North - Sand Creek System

The Sand Creek system is not protected by topography and receives drainage from oil fields in close proximity and located to the north and northwest. The maps (Figures 6, 7A) show that the sodium, chloride, and electrical conductivity levels in Sand Creek are lower than those for either Bird Creek and the Site C drainage. However, with an increase in the sensitivity of analysis, contamination levels in Sand Creek can be shown (Figure 7B) as higher than the background levels over a significant portion of its length through-out the Tallgrass Prairie Preserve. Additionally, close analysis shows that the more highly contaminated sections within the northwestern Sand Creek system actually occur in spots and are not the result of drainage from locations further to the northwest or outside the area of study.

CONCLUSIONS

The presence of significant sodium, chloride, and electrical conductivity levels in the streams and ponds within the area of study indicates that the surface waters in the Preserve have been impacted by brine contaimination. Streams transport sodium, chloride, and materials contributing to high electrical conductivity significant distances throughout the area of study. As expected, the recent brine spill (Site C) has had a more significant impact than the historic brine scars or current normal production activity.

This study is continuing with the addition of more samples and further analysis of the effects of drainage from the historic brine scars and current activity. In addition to further characterizing the pathways of brine mobility, further work will include an investigation of the effects, if any, of brine contamination on bioindicators of water quality in ponds and streams.

ACKNOWLEDGEMENT

The authors appreciate the permission, cooperation, and encouragement provided by The Nature Conservancy in pursuit of this investigation. Additionally, Mr. R.G. "Rick" Yates has received and thankfully acknowledges an EPSCOR fellowship from the Department of Energy.

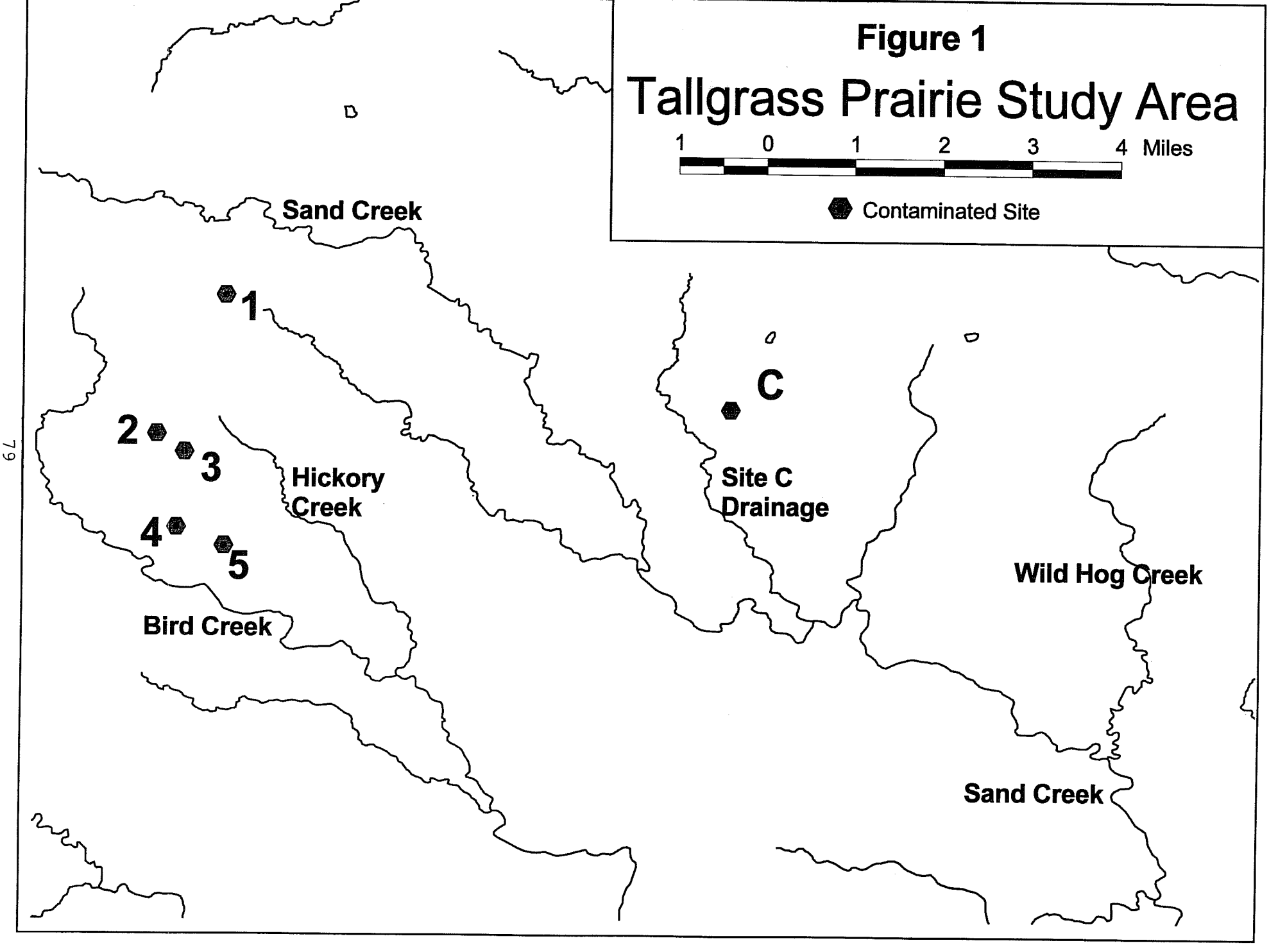
Figure 1
Tallgrass Prairie Study Area
1 0 1 2 3 4 Miles
Contaminated Site
Sand Creek
1
C
2
3
Hickory Creek
Site C Drainage
4
5
Wild Hog Creek
Bird Creek
Sand Creek

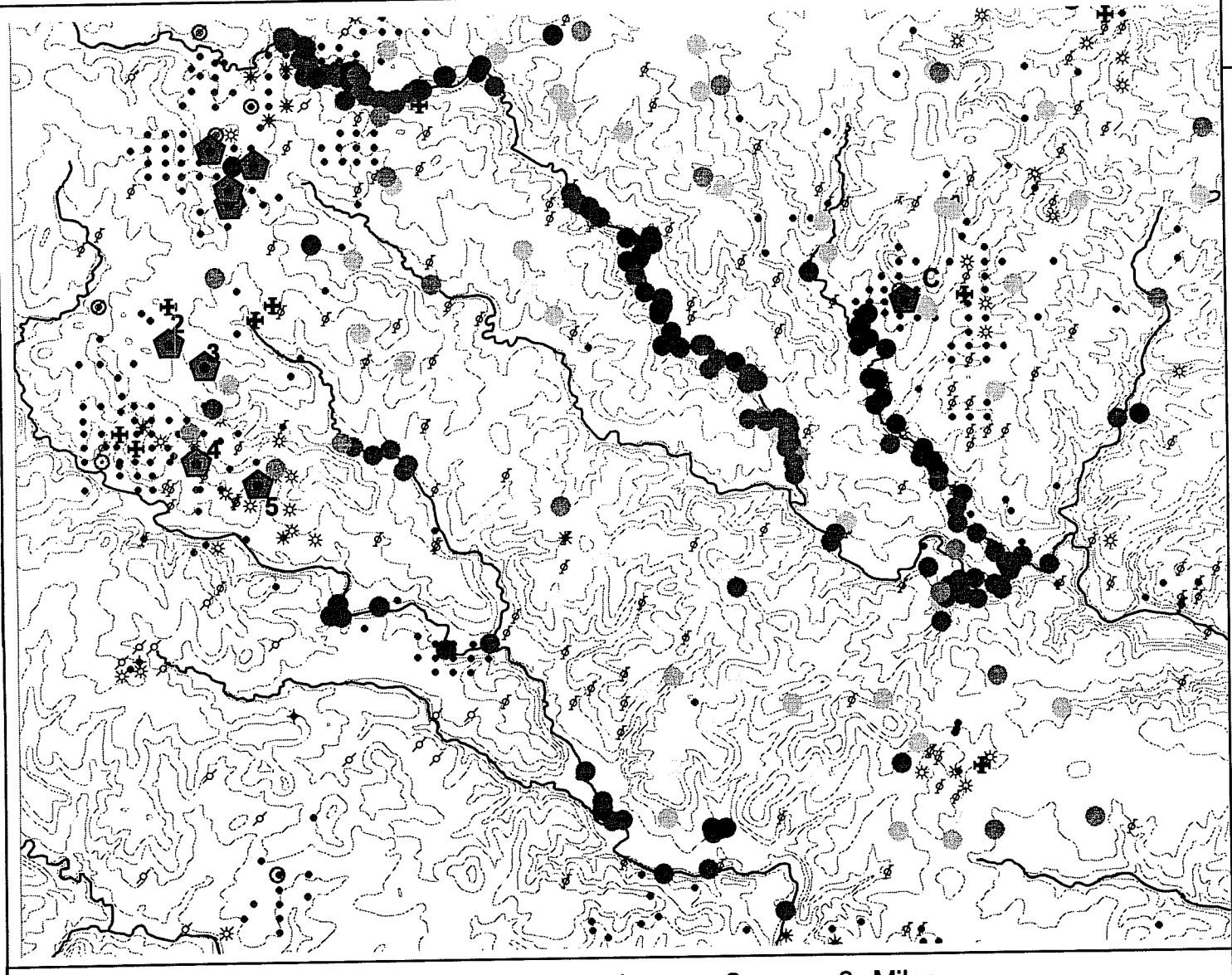

Figure 2

Electrical Conductivity (µMhos/cm)

- 0 - 100
- 100 - 200
- 200 - 300
- 300 - 400
- 400 - 500
- 500 - 1000
- 1000 - 7300

Wells

- ABANDONED
- DRY
- INJECTION
- LOC
- SERVICE
- O&G
- GAS
- OIL

Contaminated Site

1 0 1 2 3 Miles

Tallgrass Prairie - Bird Creek

Electrical Conductivity

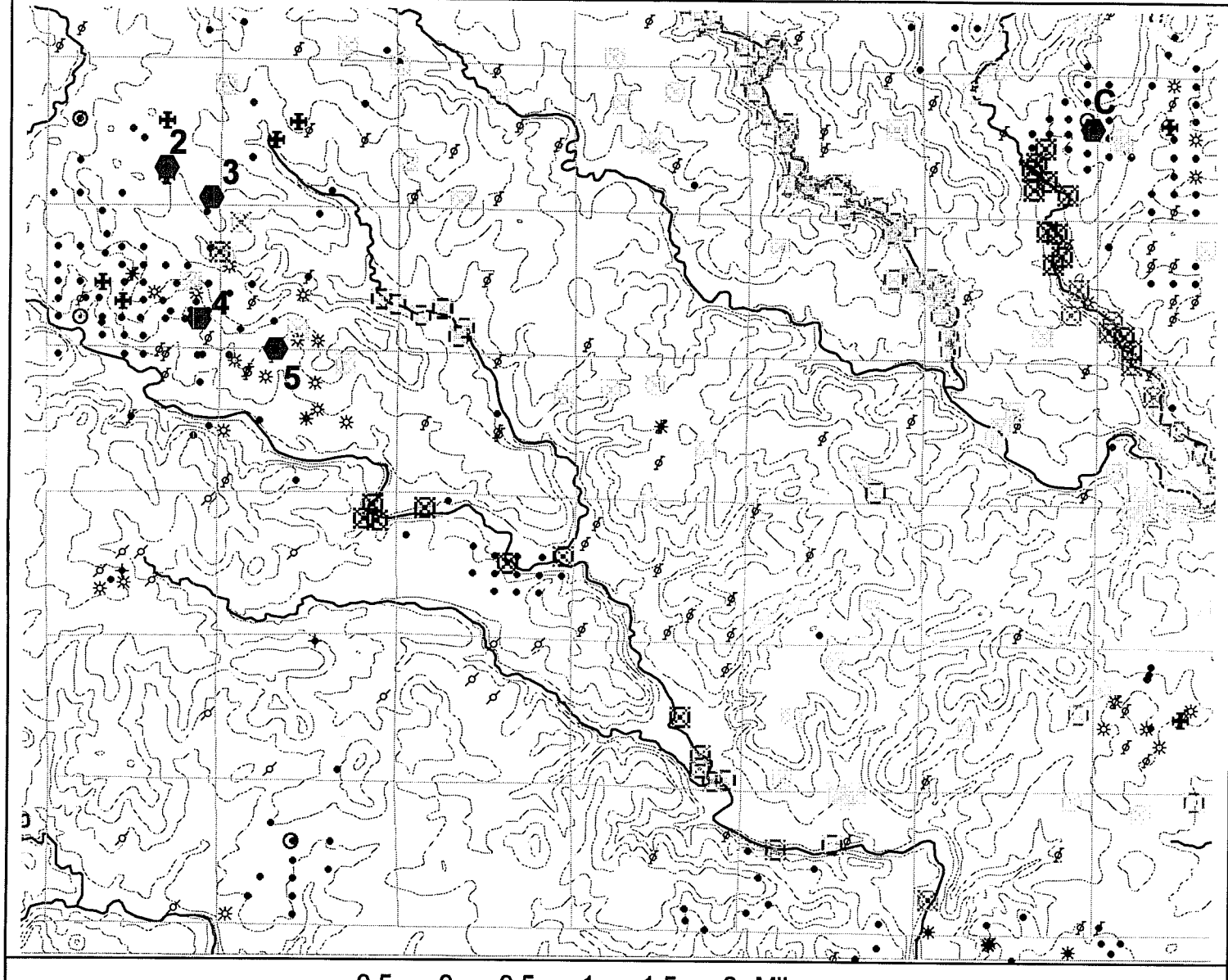

Figure 3

Chloride (ppm)
- 0 - 15
- 15 - 22
- 22 - 30
- 30 - 37
- 37 - 4164

Sodium (ppm)
- 0 - 10
- 10 - 15
- 15 - 20
- 20 - 25
- 25 - 2840

Wells
- ABANDONED
- DRY
- INJECTION
- LOC
- SERVICE
- O&G
- GAS
- OIL

Contaminated Site

0.5 0 0.5 1 1.5 2 Miles

Tallgrass Prairie - Bird Creek

Chloride and Sodium

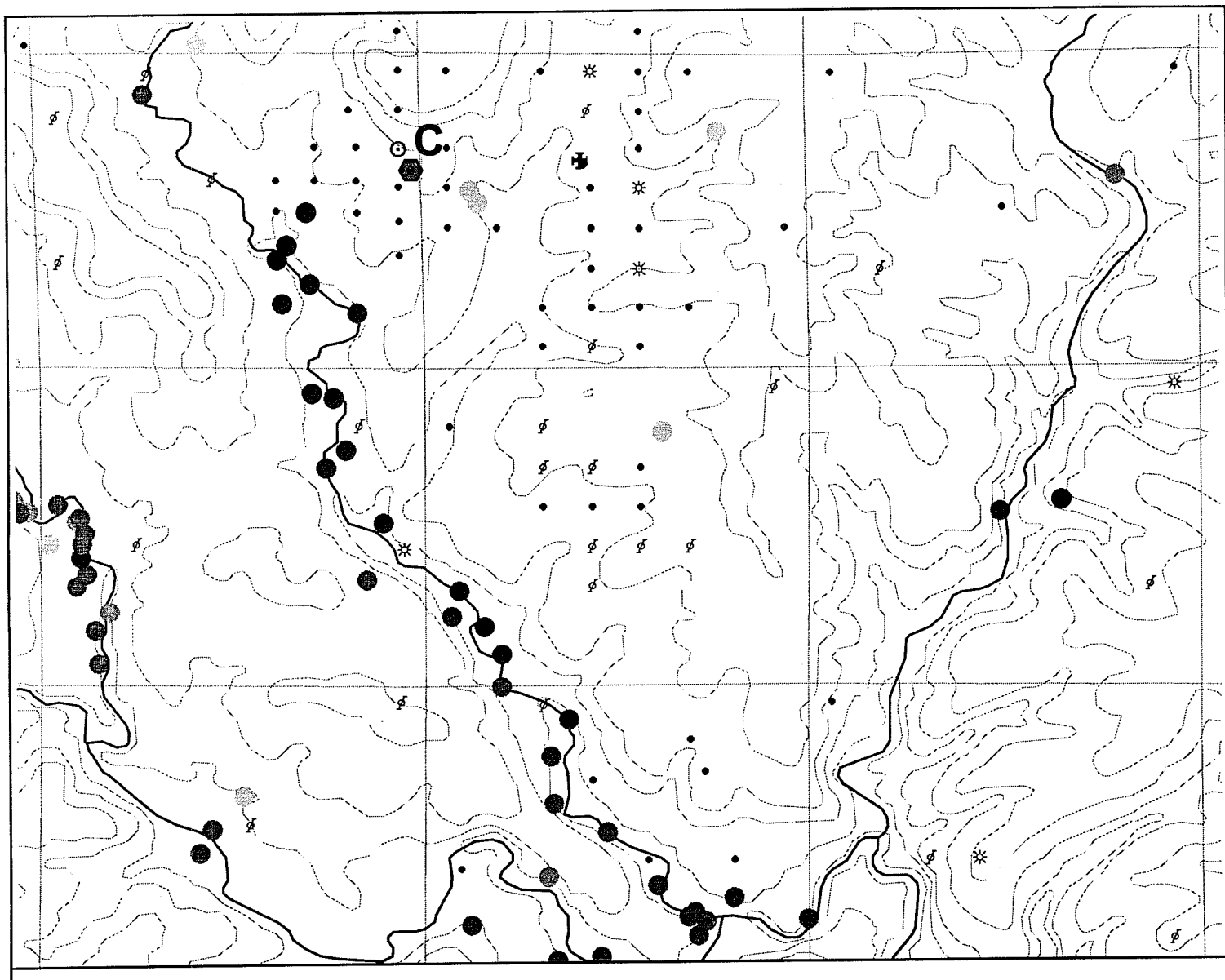

Figure 4

Electrical Conductivity (µMhos/cm)

- 0 - 100
- 100 - 200
- 200 - 300
- 300 - 400
- 400 - 500
- 500 - 1000
- 1000 - 7300

Wells

- ABANDONED
- DRY
- INJECTION
- LOC
- SERVICE
- O&G
- GAS
- OIL

Contaminated Site

Tallgrass Prairie - Spill Site C

Electrical Conductivity

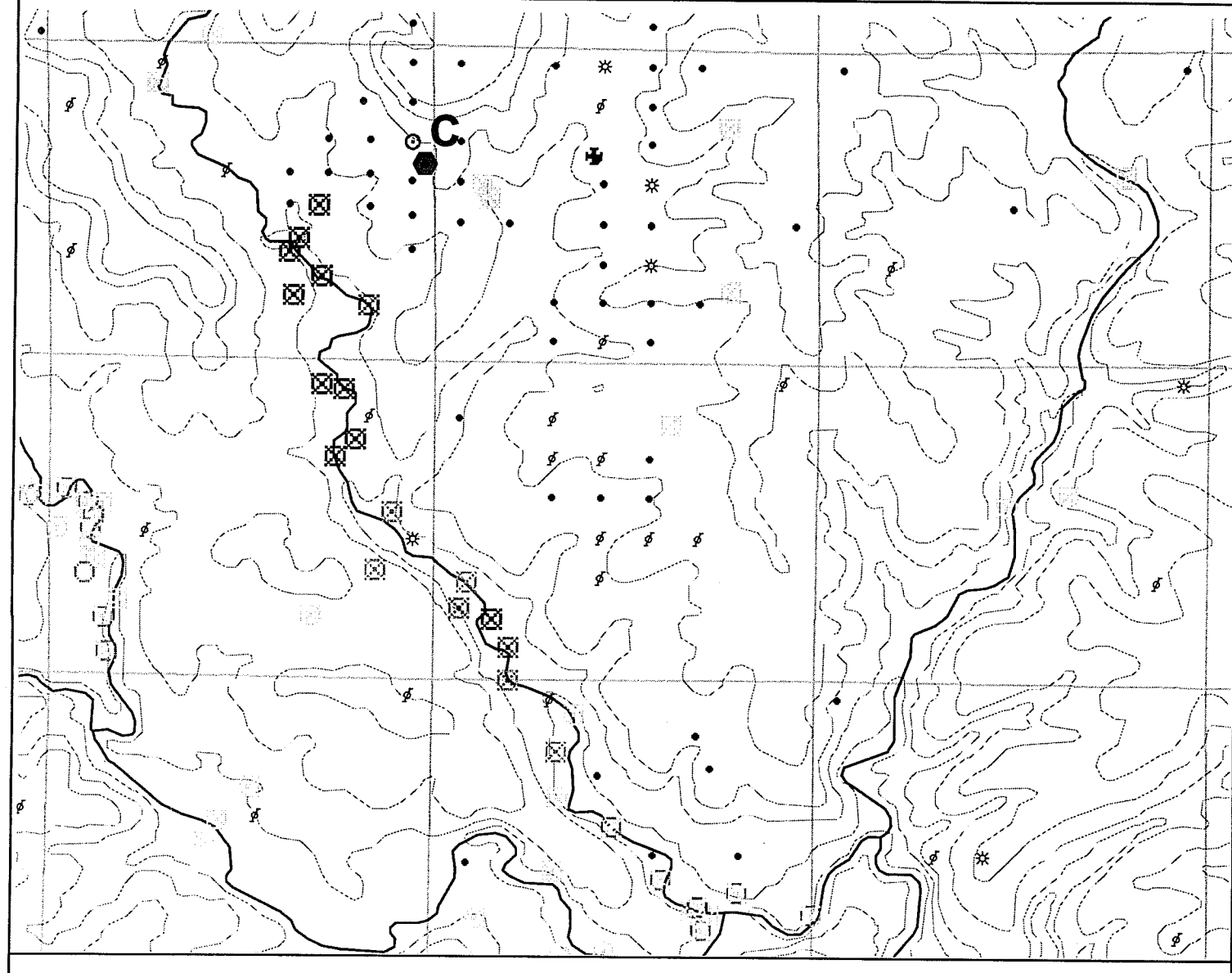

Figure 5

Chloride (ppm)
- 0 - 15
- 15 - 22
- 22 - 30
- 30 - 37
- 37 - 4164

Sodium (ppm)
- 0 - 10
- 10 - 15
- 15 - 20
- 20 - 25
- 25 - 2840

Wells
- ABANDONED
- DRY
- INJECTION
- LOC
- SERVICE
- O&G
- GAS
- OIL

Contaminated Site

0.5 0 0.5 1 Miles

Tallgrass Prairie - Spill Site C

Chloride and Sodium

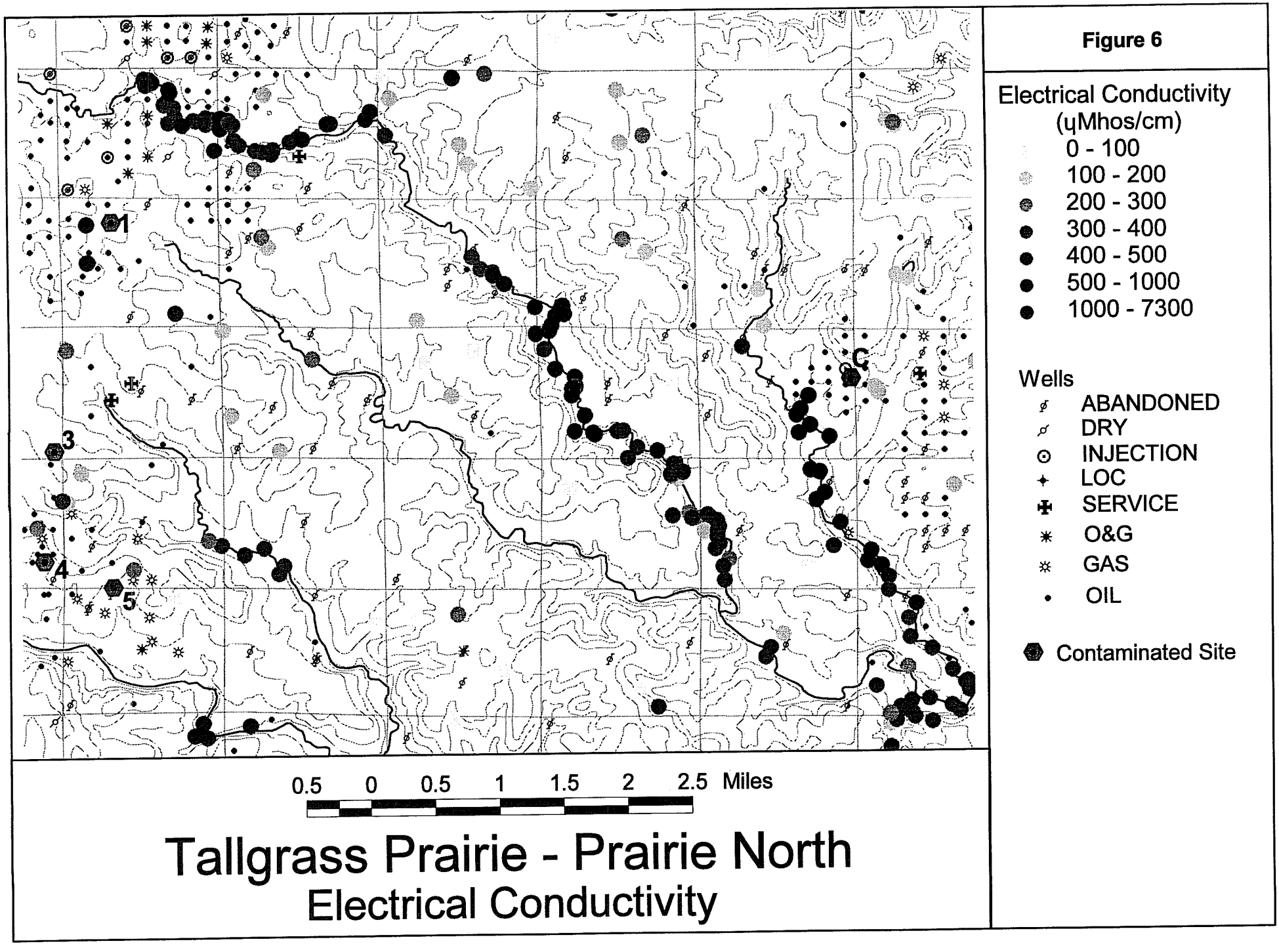
Figure 6
Electrical Conductivity (µMhos/cm)
0 - 100
100 - 200
200 - 300
300 - 400
400 - 500
500 - 1000
1000 - 7300
Wells
ABANDONED
DRY
INJECTION
LOC
SERVICE
O&G
GAS
OIL
Contaminated Site
1
3
4
5
C
0.5 0 0.5 1 1.5 2 2.5 Miles
Tallgrass Prairie - Prairie North
Electrical Conductivity

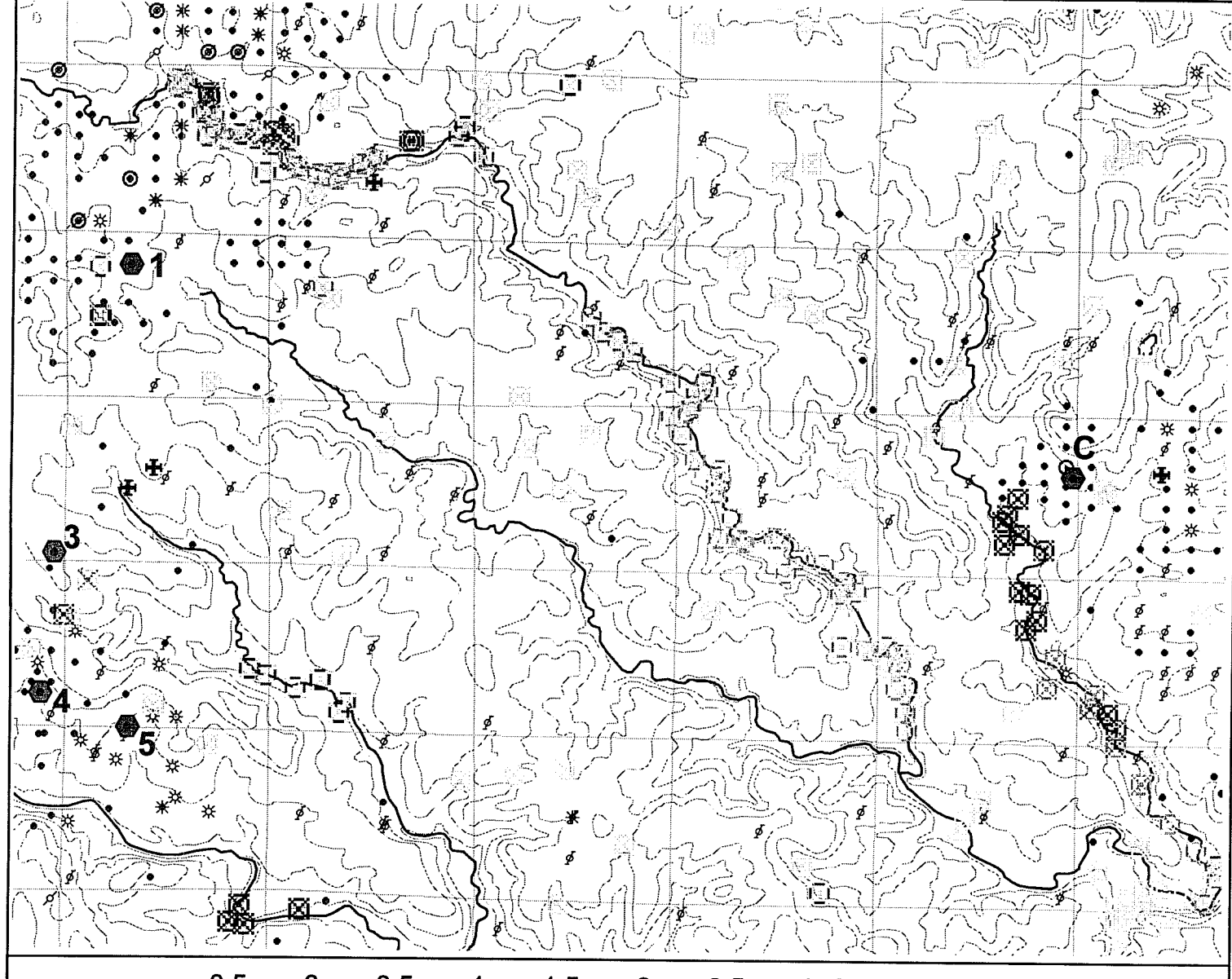

Figure 7A

Chloride (ppm)
- 0 - 15
- 15 - 22
- 22 - 30
- 30 - 37
- 37 - 4164

Sodium (ppm)
- 0 - 10
- 10 - 15
- 15 - 20
- 20 - 25
- 25 - 2840

Wells
- ABANDONED
- DRY
- INJECTION
- LOC
- SERVICE
- O&G
- GAS
- OIL

Contaminated Site

0.5 0 0.5 1 1.5 2 2.5 3 Miles

Tallgrass Prairie - Prairie North

Chloride and Sodium

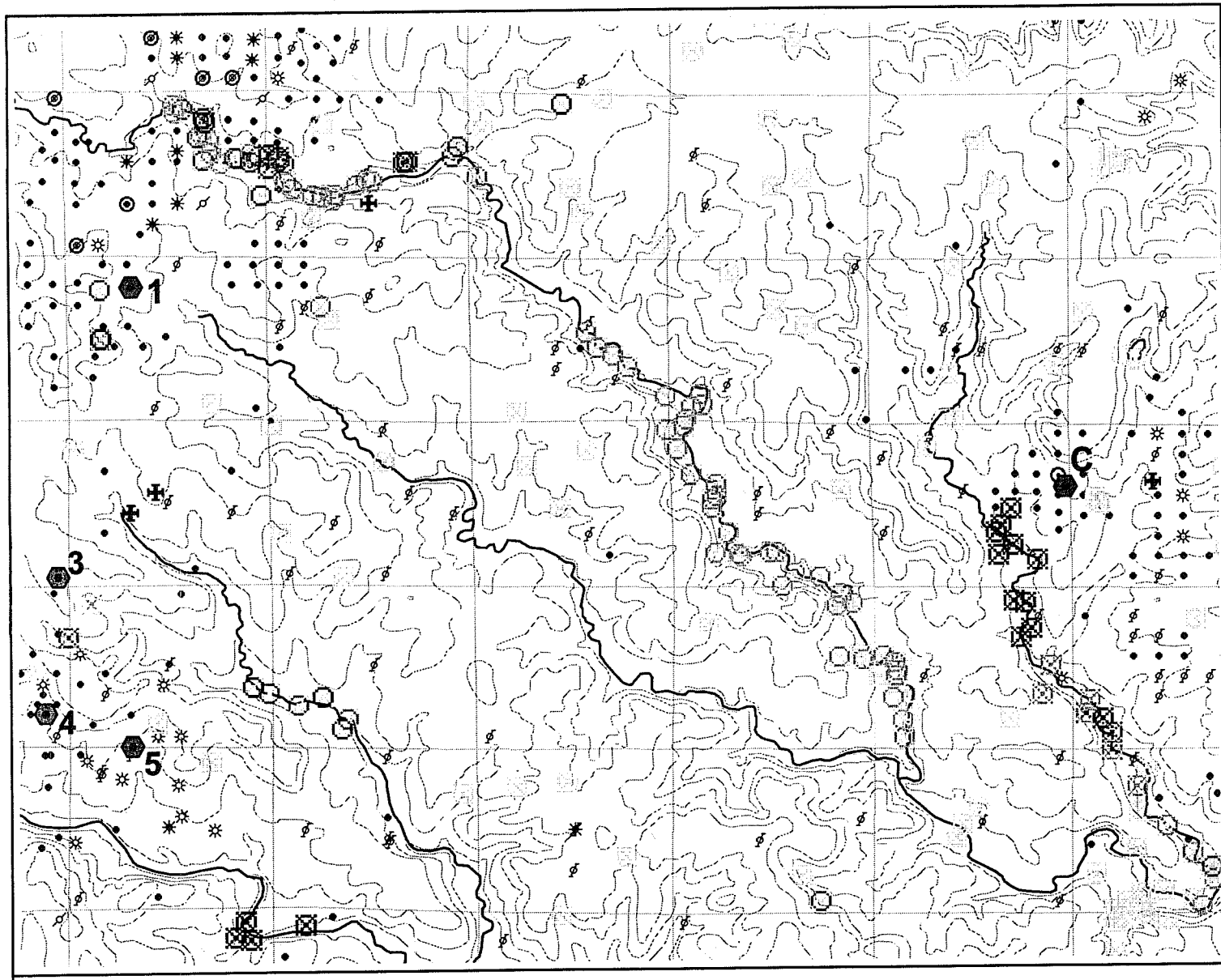

Figure 7B

Chloride (ppm)
- 0 - 5
- 5 - 10
- 10 - 20
- 20 - 30
- 30 - 4164

Sodium (ppm)
- 0 - 3
- 3 - 7
- 7 - 13
- 13 - 20
- 20 - 2840

Wells
- ABANDONED
- DRY
- INJECTION
- LOC
- SERVICE
- O&G
- GAS
- OIL

Contaminated Site

0.5 0 0.5 1 1.5 2 Miles

Tallgrass Prairie - Prairie North (low range)

Chloride and Sodium

REFERENCES

1. Harris, T.M.,"Characterization and Remediation of Brine-Impacted Soils", Encyclopedia of Environmental Analysis and Remediation, New York, John Wiley & Sons (1996).

2. Yates, R., Sublette, K., Harris, T., Tapp, B. Haggerty, J., van Waasbergen, R., and Hamilton, R., "Transport of Brine Contamination from a Recent Produced Water Spill", Proceedings of the The 3rd Petroleum Environmental Conference Tulsa, Oklahoma, Pennwell Publications (1997).

Adaptive Local Grid Modeling for Subsurface Contamination

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Modeling flow of contaminants in an aquifer requires that the computation is able to focus on areas where the chemical and physical properties of the fluids are changing. Multilevel local discretizations are designed to achieve higher accuracy in the regions where the solution's local behavior may have a significant impact on the entire domain.

In the paper we discuss the application of adaptive local grid refinement to model the contamination of an aquifer by an oil producing well. The nonaquqeous phase contaminant is assume to be immiscible in water. The aquifer is assumed to be saturated.

INTRODUCTION

The numerical modeling of multiphase fluid flow presents many computationally challenging issues. Like many other time-dependent processes, these models exhibit significant localized phenomena. The localized phenomena, such as the location of the boundary of an invading contaminant, are very important to the behavior of the chemical and physical processes.

One way to capture the behavior of the localized phenomena is to introduce a high resolution grid in the entire computational domain. Global refinement in the numerical procedure is, in general, very costly in computer time and storage due to the large number of unknowns. Local grid refinement is an elegant alternative that not only resolves the localized phenomena but also reduces the number of unknowns in the associated system of linear equations, [2, 7, 8, 6, 5, 10, 1, 9]. In local grid refinement, high resolution local grids are dynamically introduced in the regions of the computational domain where localized phenomena are crucial to the behavior of the process and coarser ones in regions that have less influence.

Modeling the boundary of an invading contaminant is a time-changing phenomenon. The localized phenomenon will change in time. High resolution grids need to be introduced or removed in response to temporal changes in the behavior of the solution. This procedure of placement/removal is recursively applied at each level of refinement until no further discretization is warranted. The final result is a composite grid consisting of local grids with various degrees of resolution. The degree of resolution increases from the coarsest grid to the finest ones. This technique is generally referred to as an *adaptive local grid refinement technique.*

The placement and removal of high resolution grids is an important part of an adaptive numerical grid method for the modeling of problems which have both a general and localized phenomena as part of the solution. Ultimately, the performance of such a method is determined by its ability in tracking as accurately as possible the localized phenomena over the domain and efficiently obtaining the numerical solution.

The key item involved is normally the choice of method for the solution of the linear systems generated by the discretization of the equations which model the flow. This issue is discussed in elsewhere, [3, 4, 4]. This paper focuses on the application of adaptive local grid refinement to model invading oil contamination in a saturated aquifer.

MODELING EQUATIONS

In the paper we discuss the application of adaptive local grid refinement to model the contamination of an aquifer by an oil producing well. The nonaquqeous phase contaminant is assume to be immiscible in water. The aquifer is assumed to be saturated.

We consider an oil well that is contaminating an aquifer by leaking in certain zones of the aquifer. To construct the model we consider a cylindrical portion of the aquifer around the polluting well. The contaminant model simulates the leaking of oil from a producing well into a saturated aquifer. The mathematical formulation for the model problem is derived by making the following assumptions:

- The aquifer is filled with water which is assumed to be a slightly compressible fluid,
- the invading oil is also assumed to be a slightly compressible fluid,
- viscosity, capillarity, and gravity effects control the fluid flow,
- the bottom and top boundaries of the aquifer are sealed to flow.
- the outer boundary of the aquifer is sealed to flow.

The following pair of diffusion-transport equations describe the fluid flow of the water phase and the contaminant oil-phase in the aquifer. The equations are given in cylindrical coordinates:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{k_r k_{rl}}{B_l\mu_l}\frac{\partial\Phi_l}{\partial r}\right)+\frac{\partial}{\partial z}\left(\frac{k_z k_{rl}}{B_l\mu_l}\frac{\partial\Phi_l}{\partial z}\right)=\frac{1}{5.615}\frac{\partial}{\partial t}\left(\frac{\phi s_l}{B_l}\right), \tag{1}$$

where the subscript $l = o, w$ refers to the oil and water phases, respectively; k_r and k_z are the absolute permeabilities in the r- and z-direction, respectively; s_l is the phase saturation; k_{rl} is the relative permeability; μ_l is the viscosity; B_l is the formation volume factor; ϕ is the porosity and Φ is the flow potential.

Let r_w be the radius of the well and r_e be the external radius of the aquifer. Also let p_l be the phase pressure and q_t be the total injection rate. The associated initial and boundary conditions satisfying the above assumptions are described as follows:

- Initial condition:

$$\Phi_l|_{t=0} = \Phi_{li},$$

- the outer boundary of the aquifer is sealed (no-flow boundary):

$$\frac{\partial\Phi_l}{\partial r}|_{r=r_e} = 0,$$

- the inner boundary conditions (partial perforation between h_t and h_b):

$$\frac{\partial \Phi_l}{\partial r}|_{r=r_w} = 0, \qquad z > h_b,$$

$$\frac{\partial \Phi_l}{\partial r}|_{r=r_w} = 0, \qquad z < h_t,$$

$$2\pi r_w \int_{h_t}^{h_b} \left(\frac{k_r k_{ro}}{B_o \mu_o} \frac{\partial \Phi_o}{\partial r} + \frac{k_r k_{rw}}{B_w \mu_w} \frac{\partial \Phi_w}{\partial r} \right)_{r_w} dz = q_t. \tag{2}$$

- the top boundary of the aquifer is sealed (no-flow boundary):

$$\frac{\partial \Phi_l}{\partial z}|_{z=0} = 0,$$

- the bottom boundary of the aquifer is also sealed (no-flow boundary):

$$\frac{\partial \Phi_l}{\partial z}|_{z=z_b} = 0,$$

- the saturation constraint is given by

$$s_o + s_w = 1, \tag{3}$$

- the pressure difference between the two phases is described by the capillary pressure:

$$p_c = p_o - p_w, \tag{4}$$

- the potentials are defined as

$$\Phi_o = p_o - \frac{1}{144} \frac{g}{g_c} \rho_o z, \tag{5}$$

$$\Phi_w = p_o - \frac{1}{144} \frac{g}{g_c} \rho_w z - p_c, \tag{6}$$

where g is the gravity acceleration, g_c is the concentration factor, and ρ_l is the phase density.

A cross section of the aquifer showing multiple layers and the polluting well is shown in Figure 1.

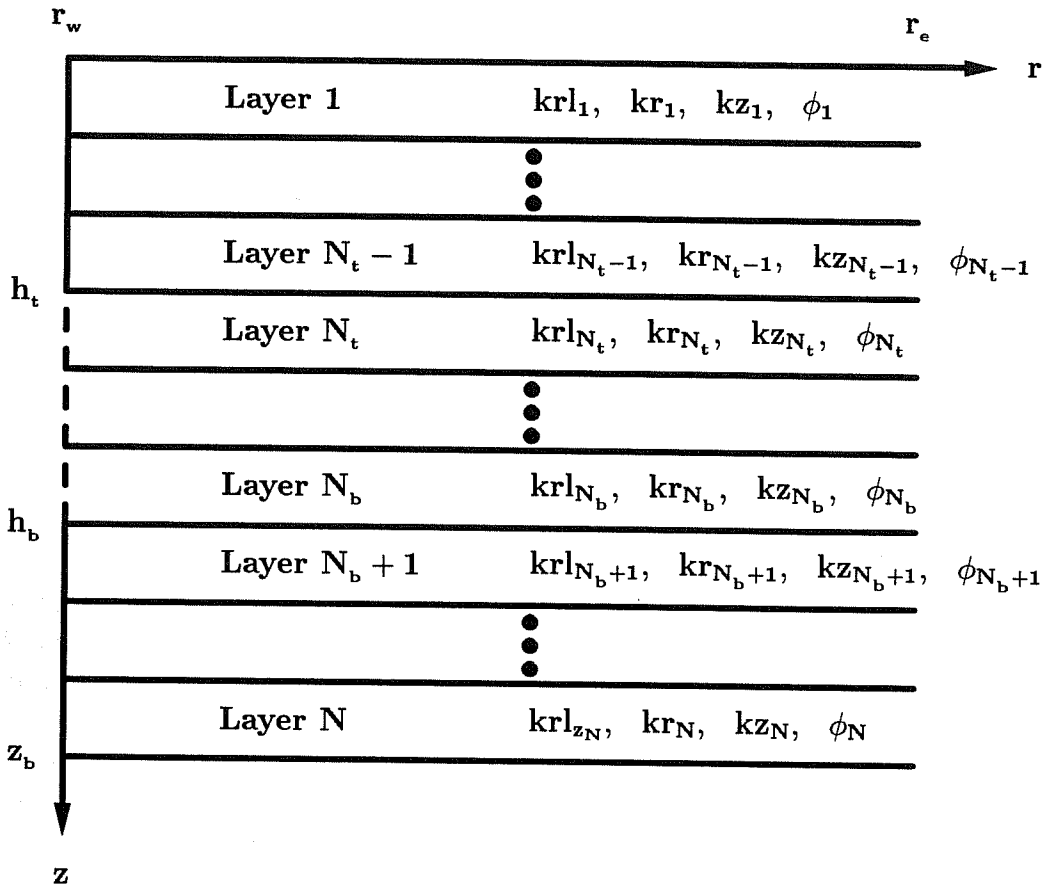

Figure 1: Cross sectional model of aquifer. The dashed lines indicate the zone in which the producing oil well leaks into the aquifer.

APPLICATION OF ADAPTIVE GRID REFINEMENT

The physical properties of the aquifer and well are:

Depth of formation : 4000 ft
Initial pressure in bottom layer : 1000 psi
Initial bottom hole pressure : 1000 psi
Contamination rate from well : 5000 std/day
Irreducible water saturation : 0.15
Wellbore radius : 0.5 ft
Radial extent of aquifer : 3000 ft
Compressibility of oil : 1.0e-6 psi^{-1}
Compressibility of water : 1.0e-6 psi^{-1}
Viscosity of oil, μ_o : 2.0 cp
Viscosity of water, μ_w : 0.4 cp

Table 1: PVT Table for Oil and Water

Pressure	B_o	ρ_o	B_w	ρ_w
14.7	1.300	51.54	1.150	61.74
264.7	1.297	51.67	1.149	61.79
514.7	1.294	51.80	1.148	61.83
1014.7	1.287	52.06	1.147	61.92
2014.7	1.274	52.58	1.143	62.11
2514.7	1.268	52.84	1.141	62.20
3014.7	1.262	53.11	1.140	62.30
4014.7	1.249	53.64	1.136	62.48
5014.7	1.237	54.18	1.123	62.67
9014.7	1.218	56.39	1.128	63.13

Table 1 gives the PVT data for oil and water; B_o, and ρ_o correspond to the volume factor, and density of the oil phase, respectively, while B_w, and ρ_w correspond to the volume factor, and density of the water phase, respectively. The relative permeability and capillary data for the oil-water system is given in Table 2; S_w, K_{rw}, and K_{ro} correspond to saturation of water phase, relative permeability of water phase, and relative permeability of oil phase.

The porosities and permeabilities are assumed constant throughout the aquifer; the permeability along the $r-$direction is 100 md, the permeability along the $z-$direction is 20 md, and the porosity is 0.1.

EXPERIMENTS

The coarsest grid employed was a 10×10 grid with a height of 30 ft for the coarse grid layers. The simulation was run without local refinement and with one-level of refinement where the local grids are 3×3 grids. Figure 2 shows the saturation profiles in the 5th layer of the coarse grid. Qualitatively speaking, the one-level discretization gives a more appealing curve near the "front".

The one-level adaptive approximation was calculated at a cost which is not much greater than the cost for using the coarse grid. In order to ascertain the quality of this approximation, we computed the solution for a 30×30 grid which has grid blocks which are the size of the smallest grid

Table 2: Relative Permeability

S_w	K_{rw}	K_{ro}
0.1500	0.0000	0.9500
0.2000	0.0040	0.7500
0.2500	0.0102	0.5876
0.3000	0.0166	0.4462
0.3500	0.0232	0.3325
0.4000	0.0305	0.2450
0.4500	0.0395	0.1770
0.5000	0.0497	0.1200
0.5500	0.0630	0.0724
0.6000	0.0798	0.0374
0.6500	0.0800	0.0274
0.7000	0.0850	0.0174
0.7500	0.0868	0.0090
0.8000	0.0900	0.0074
0.8500	0.0910	0.0060

blocks used in the one-level adaptive scheme. The cost of the 30×30 is much higher than the one-level simulation. Figure 3 again shows the saturation profiles in the 5th layer of the coarse grid. The one-level adaptive scheme gives a solution which matches well with the solution given by using a fine, global grid but at a fraction of the cost.

Another simulation was run with a two-level refinement. The cost of this simulation was lower than the global 30×30 simulation. Figure 4 shows the saturation profiles in the 5th layer of the coarse grid. Again, the two-level discretization gives a more appealing solution near the "front." Because of the time and resources required for the simulation, we were unable to run a global refinement of 90×90 which would have given the same degree of accuracy as the two-level refinement.

CONCLUSION

The possibility to focus the calculations in an area of importance to the overall numerical solution is illustrated. Figure 5 compares the two-level local refinement with uniform 10×10 and 30×30 refinements. The quality of the two-level solution is evident in the Figure. The two-level solution cost less to compute than the 30×30 uniform refinement.

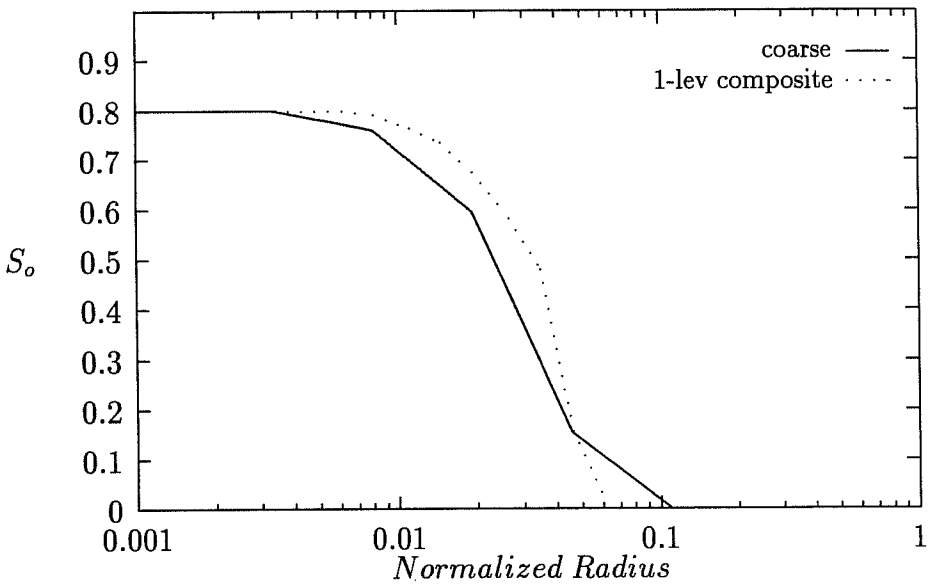

Figure 2: Saturation profile in the 5th layer of the coarse grid; coarse grid vs. one-level local grid.

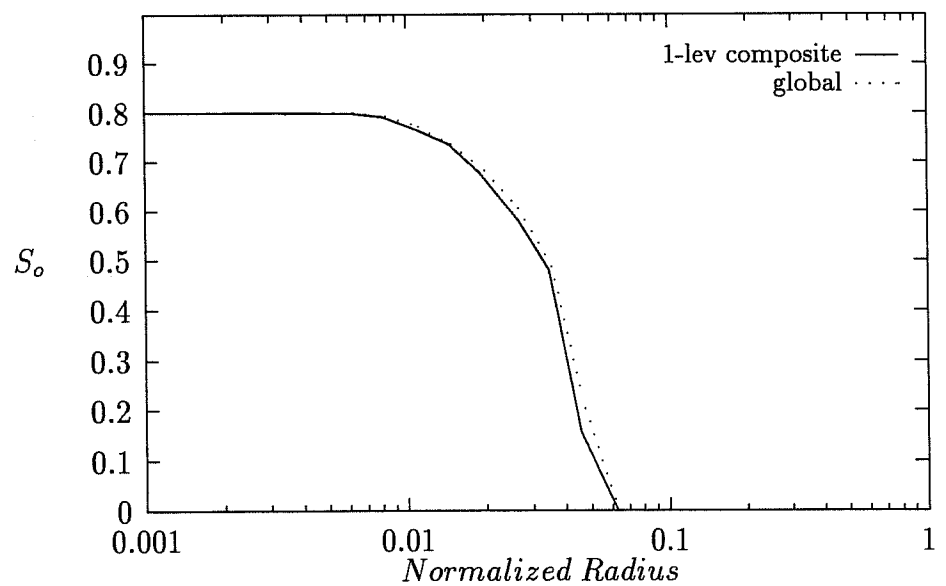

Figure 3: Saturation profile in the 5th layer of the coarse grid; global grid vs. one-level local grid.

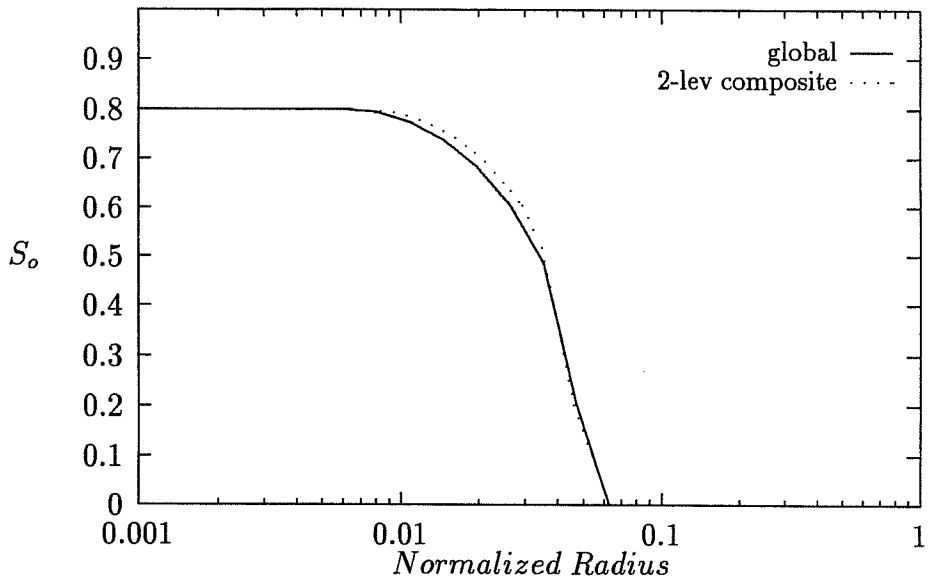

Figure 4: Saturation profile in the 5th layer of the coarse grid; global grid vs. two-level local grid.

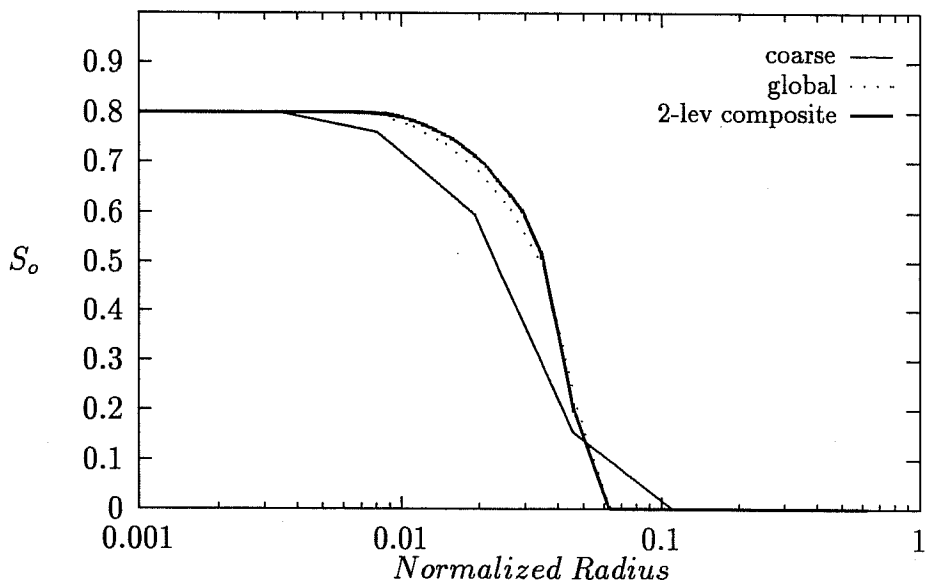

Figure 5: Saturation profile in the 5th layer of the coarse grid; coarse, global, and two-level local grids.

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An Adaptive Grid Technique With Smoothing for Minimizing Heterogeneity in Elements

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New approaches to hydrologic modeling, such as geostatistics, allow simulation of the natural heterogeneity of properties such as porosity or hydraulic conductivity. The property simulations can be carried out at a fine scale while porous media flow modeling typically requires a coarser scale. Numerical errors are introduced by approximating hydrologic properties at the coarser scale. Adaptive gridding can be used to allow the coarser grid to capture more of the details in the property simulations and reduce the numerical errors. A geostatistical adaptive grid (GAG) algorithm is presented that is based on local minimization of heterogeneity within each element of the flow grid. Local minimization also allows control of the distortion of the elements while generating the grid. A smoothing algorithm allows distortion to be controlled in areas of the grid where the heterogeneity has been sufficiently reduced.

INTRODUCTION

Geologic materials are inherently heterogenous and contain a great deal of structure. Heterogeneity can be important to flow processes that result in early break-through in enhanced oil recovery techniques or lower residence times in contaminate transport. Where such flow processes are important, heterogeneity should be included in the numerical models.

Geostatistical approaches and other methods are becoming more adept at simulating the heterogeneity of the hydrologic properties. These methods allow a description of a domain in a relatively fine degree of detail, often consisting of millions of nodes. Flow modeling is typically carried out at a coarser scale due to computational constraints. Despite the coarser grid, it is important to capture as much of the geologic structure as possible. Since hydrologic property simulation often produces many realizations for a Monte Carlo method, the flow grid also must be generated automatically.

SOURCE OF NUMERICAL ERRORS

Heterogeneity affects the convergence rate of numerical methods for porous media flow. Numerical methods that are not aware of the geometry of the elements (such as network flow models) generally are first order. Some of these methods can employ Voronoi grids to increase their order of convergence. Methods that are aware of the geometry of the element typically have a second order convergence rate (or higher). However, there are several factors that can reduce these higher order convergence rates.

1) If a method uses a constant hydraulic conductivity for each element the convergence rate will only be first order where the errors due to the variation of the conductivity are not dominated by geometrical errors.
2) If the hydraulic conductivity is discontinuous then unless the discontinuity is located at special locations, typically the edges between elements, the convergence rate will be first order (1).
3) The convergence rate will not exceed the smoothness of the actual solution; where the solution is discontinuous the convergence rate will be first order (2).

The first factor can be avoided by using numerical methods that are designed correctly. The second factor can be greatly mitigated by using an adaptive grid that locates the edges of the elements along the discontinuities of the hydraulic conductivity. The third factor is unavoidable, although the first order convergence

can be limited to small parts of the domain where the solution is discontinuous including reducing the size of elements generated by using adaptive grids.

Heterogeneous media has properties that exhibit a dependency on scale of the sample. Determining an appropriate value for a property of an element based on the values at a smaller scale given by the geostatistical simulation has the potential for a large amount of error. An adaptive grid can reduce these errors by reducing the variation of the property (heterogeneity) within an element.

Using adaptive gridding can reduce numerical errors, but highly distorted grids can introduce errors of their own. The effects depend on the particular finite element or finite difference scheme. In general, the convergence rate will not be affected if there is some bound on the distortion of the grid as the grid is refined. Another consideration is whether the numerical method will reach a solution if the grid is very distorted. For these reasons, a method for user-specified smoothing of an adaptive grid is desired.

MEASURES OF HETEROGENEITY

Once the heterogeneity of an element is defined, a vector of values is obtained consisting of the heterogeneity of each element. One definition of the heterogeneity is the standard deviation of the property, σ. Heterogeneity over the problem domain also is dependent on the area. In addition, truncation errors introduced by numerical flow calculations are expressed in terms of the size of the element. Thus, the heterogeneity of an element is defined as $\sigma_i a_i$ where a_i is the area of the ith element.

Two commonly used measures of a vector are the 2-norm and ∞-norm

$$\|\sigma \mathbf{a}\|_\infty \equiv \max_{1 \le i \le n} \sigma_i a_i, \tag{1}$$

$$\|\sigma \mathbf{a}\|_2 \equiv \left[\sum_{i=1}^{n} (\sigma_i a_i)^2 \right]^{1/2} \tag{2}$$

The ∞-norm is more sensitive to extreme values of the heterogeneity while it may not be affected by improvements of the mesh in regions where there are smaller values of heterogeneity. Since the ∞-norm measures the maximum heterogeneity, it is useful to bound the upscaling error. The 2-norm incorporates the heterogeneity of all the elements in its measure and thus is a better norm in reducing total upscaling errors. The ways in which these norms can be reduced is

1) Aligning adjacent elements with the geologic structure. Or by reducing the size of heterogeneous elements which may allow smaller geologic structures to be captured in heterogeneous regions.
2) Adjusting elements where the domain is inherently heterogeneous such that the area is inversely proportional to the standard deviation. High standard deviations are constrained to small elements where they presumably have less effect on the numerical flow code.

GEOSTATISTICAL ADAPTIVE GRID (GAG)

The adaptive grid problem is a nonlinear optimization problem of redistribution of a fixed number of nodes, called *R*-type adaptivity. One approach is to cast the problem as an nonlinear elliptic grid generator by assigning elasticities to the edges connecting the nodes of the mesh based on the heterogeneity of the neighboring elements (3). Another approach is a direct optimization grid generator using simulated annealing (4). GAG is a direct optimization approach that uses local minimization, recognizing that heterogeneity is largely a local phenomena.

GAG is based on direct reduction of the norm $\|\mathbf{w}\sigma\mathbf{a}\|_2$ where $\mathbf{w}$ is a user-specified vector of weights (omitted from the following formulas without loss of generality). For a node l, define σ_l and $\mathbf{a}_l$ as vectors containing the standard deviation and area, respectively, of the neighboring for elements or cells. The difference

$$\|\boldsymbol{\sigma}^{t+1}\mathbf{a}^{t+1}\|_2^2-\|\boldsymbol{\sigma}^{t}\mathbf{a}^{t}\|_2^2=\|\boldsymbol{\sigma}_J^{t+1}\mathbf{a}_J^{t+1}\|_2^2-\|\boldsymbol{\sigma}_J^{t}\mathbf{a}_J^{t}\|_2^2, \tag{3}$$

only involves four elements to determine whether moving a node improves a grid. The computation should be local to be tractable, so the data should be accessible by flow element. Thus, a list is set up for each element containing geostatistical nodes within that element. The lists are dynamic, allowing geostatistical nodes to be moved between the four neighboring elements as a node of the flow grid is moved. Computing Equation 3 then requires accessing the lists of only four elements.

The grid adaption process is given by

1) Create an initial grid.
2) Set up lists of geostatistical nodes belonging to each element.
3) Calculate σ_l and $\sigma_i a_i$ for each element.
4) Iterate over the following while nodes are still being moved.

a) Calculate the local norm for each node in the flow grid.
b) Perform sort to order the flow grid nodes in decreasing order of local norms.
c) Iterate over nodes in flow grid.
    i) Move node and recompute local norm.
    ii) Accept or reject move.
    iii) If accepted, store new σ_i, $\sigma_i a_i$, local norms and lists assigning geostatistical nodes.

There are an infinite number of possibilities for directions and step sizes for moving the nodes in the flow grid. However, the geostatistical grid imposes a minimum discrete step size on the problem; take a step smaller than the spacing in the geostatistical grid and there is no guarantee that any geostatistical nodes will change elements. In addition, the geostatistical grid represents the maximum resolution of the flow problem. Thus, GAG moves each node in the four principal directions with a step size equal to the underlying spacing of the geostatistical grid. Note that it is possible using the four component values of the local norm to predict which direction the node should move although this has not been attempted in GAG.

There are many ways to generate an initial grid for GAG. The method currently implemented is an algebraic method based on linear interpolation. Boundary nodes also do not have to be fixed but are allowed to slide along specified boundary functions with only the four corner nodes that join these boundaries fixed (5).

CONTROL OF DISTORTION

GAG can produce very distorted grids which may not be acceptable for use in numerical flow simulators. Fortunately, the local nature of the grid adaption used in GAG allows element shape requirements to be easily incorporated when the decision to accept or reject a move is made.

Both finite element and finite difference methods on irregular grids typically use a mapping from physical space to a master element or logical space. The Jacobian of the transformation, $|\mathbf{J}|$, must be greater than 0 to ensure that the mapping is one-to-one; otherwise the mapping is degenerate. A physical interpretation for quadrilateral elements is that the quadrilateral must be convex; i.e., no angles of greater than 180°. For finite elements, basis functions are employed to define the mapping. For quadrilateral elements with bilinear basis functions, the Jacobian is

$$|\mathbf{J}| = j_0 + j_1\xi + j_2\eta, \tag{4}$$

where ξ and η are local coordinates of the master element and

$$\begin{aligned} j_0 &= [(x_1 - x_3)(y_2 - y_4) - (x_2 - x_4)(y_1 - y_3)]/8, \\ j_1 &= [(x_3 - x_4)(y_1 - y_2) - (x_1 - x_2)(y_3 - y_4)]/8, \\ j_2 &= [(x_2 - x_3)(y_1 - y_4) - (x_1 - x_4)(y_2 - y_3)]/8, \end{aligned} \tag{5}$$

and the corners (x_i, y_i) of the quadrilateral are numbered counterclockwise. Thus the condition for avoiding degenerate mappings is

$$j_0 - |j_1| - |j_2| > 0. \tag{6}$$

The condition implemented in GAG to prevent excessive distortion is

$$\frac{j_0 - |j_1| - |j_2|}{j_0} > 0.1. \tag{7}$$

The condition given by Equation 7 requires that stretching within an element vary by less than an order of magnitude.

Smoothing can be applied throughout the grid by adding a functional based on local control. Define the vector

$$\mathbf{j} \equiv \left[\frac{|(j_1)_1| + |(j_2)_1|}{(j_0)_1}, \ldots, \frac{|(j_1)_n| + |(j_2)_n|}{(j_0)_n} \right]^T, \tag{8}$$

and the vector $\mathbf{j}_l$, which contains only the entries for the neighboring four elements. Note that from the condition given by Equation 6 that the entries of $\mathbf{j}$ lie between 0 and 1. Define $(\sigma_l \mathbf{a}_l)_{\min}$ as the minimum value of the local vector and the constant $C = \min((\sigma_l^{t+1}\mathbf{a}_l^{t+1})_{\min}, (\sigma_l^t \mathbf{a}_l^t)_{\min})$. Then the local functional used for accepting a move is defined as

$$\|\boldsymbol{\sigma}_J^{t+1}\mathbf{a}_J^{t+1}\|_2 + \alpha C\|\mathbf{j}_J^{t+1}\|_2 < \|\boldsymbol{\sigma}_J^t \mathbf{a}_J^t\|_2 + \alpha C\|\mathbf{j}_J^t\|_2, \tag{9}$$

where the user-specified $\alpha \in [0,1]$. As heterogeneity is resolved, $\sigma_i a_i$ approaches equal distribution and for $\alpha = 1$ the two terms become of equal magnitude for

highly distorted elements. Thus elements in areas where the heterogeneity is resolved tend to be smoothed. For early iterations or where heterogeneity is not resolved, the first term dominates the second term and resolving heterogeneity takes precedence. The local nature of the test allows smoothing to be treated differently throughout the mesh based on how well the heterogeneity has been resolved.

EXAMPLES

The geostatistical simulation for Example 1 is a slice from a three dimensional indicator simulation of an alluvial fan deposit with some diagenesis (6). There are seven indicators representing different hydrologic facies. The geostatistical grid is 81 x 61 upon which an 11 x 11 flow grid is overlaid. GAG reduces $\|\sigma \mathbf{a}\|_2$ 28% and produces the grid shown in Figure 1 for $\alpha = 0$. Figure 2 compares the initial and final element standard deviations.

Figure 1. Grid for Example 1.

Example 2 is a slice from a three dimensional simulation of porosity of volcanic tuffs lying above the water table at Yucca Mountain, Nevada. Indicator simulation is used to generate the hydrologic units and Gaussian simulation generates unconditional spatially correlated porosities within the hydrologic units. The upper surface is the topographic surface while the bottom is the water table. The higher porosity band in the upper part of the example is the nonwelded

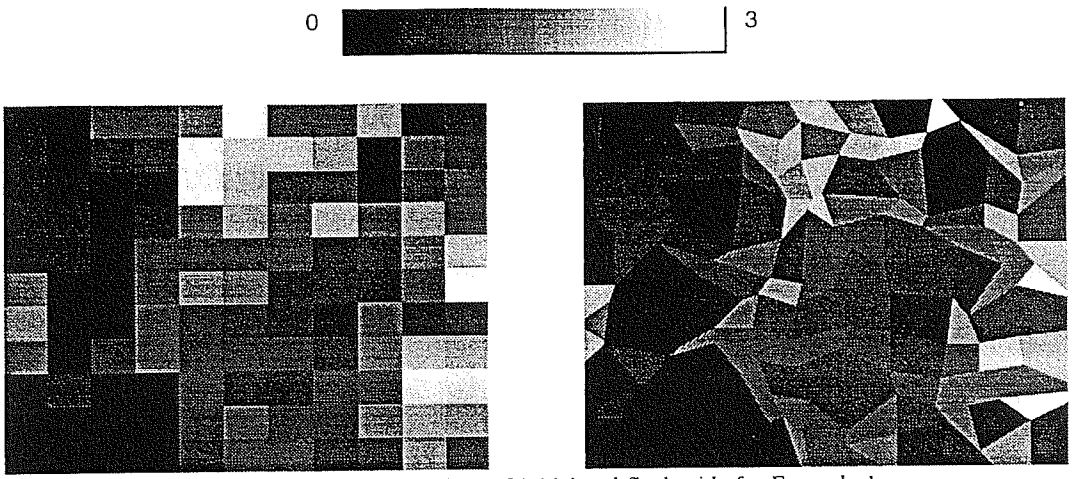

Figure 2. Standard deviations of initial and final grids for Example 1.

Paintbrush. The grid is weighted to concentrate elements beneath the nonwelded Paintbrush outcrop and place a row of smaller elements at the surface. Figures 3, 4 and 5 show the resulting grid for three values of α. For α=0 and 0.5 the reduction in the 2-norm is 32% and 31%, respectively. For α=1 the reduction in the 2-norm is affected by the smoothing but still is 25%.

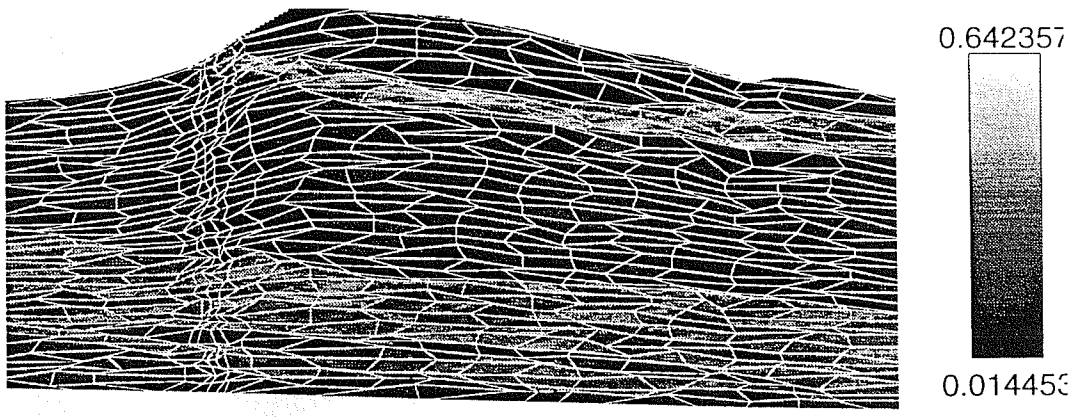

Figure 3. Adaptive grid with α = 0 for Example 2.

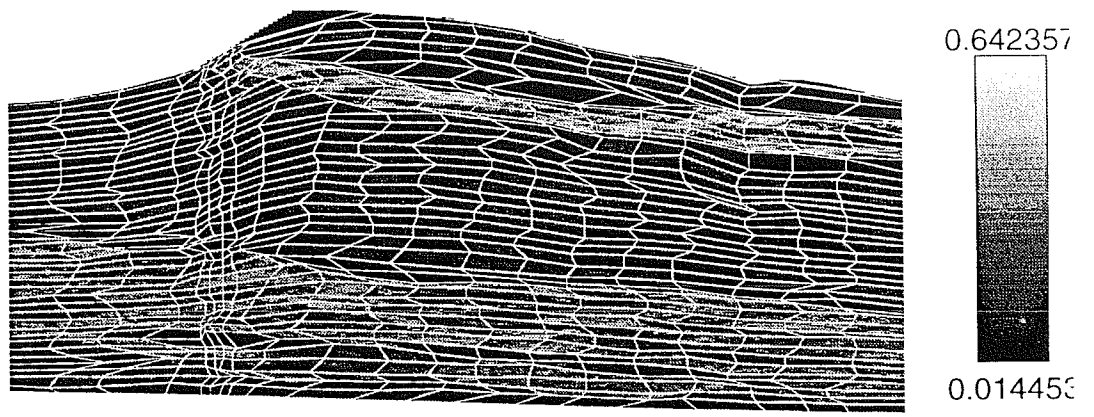

Figure 4. Adaptive grid with α = 0.5 for Example 2.

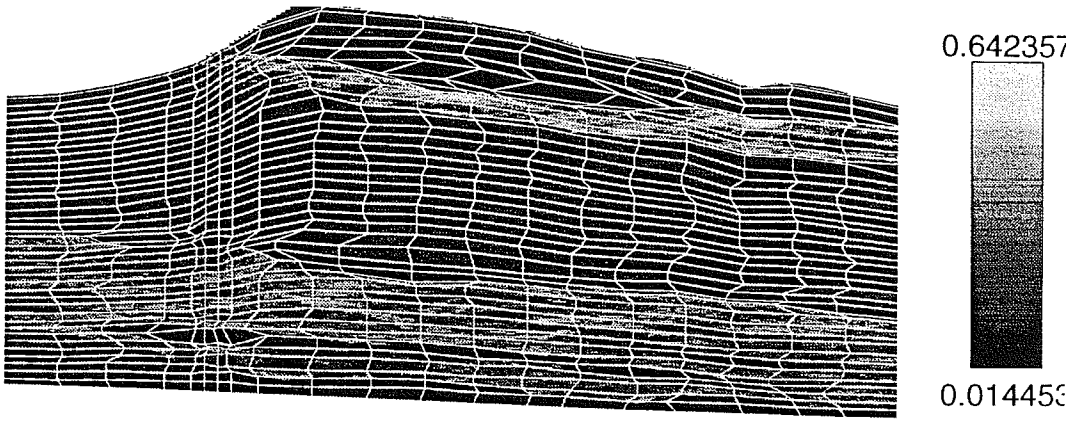

Figure 5. Adaptive grid with $\alpha = 1$ for Example 2.

CONCLUSION

Adaptive gridding can greatly increase the accuracy of numerical methods. For highly heterogeneous media, second order convergence cannot be achieved without adaptive gridding. Also geometric details can be captured and upscaling errors reduced.

GAG generates grids that show significant reduction of heterogeneity. Element size tends to be reduced in areas of high heterogeneity. Smoothing can be applied to the grid without significantly affecting the reduction of heterogeneity.

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Application of Inverse Problem Theory to Estimate Initial Source Parameters in Subsurface Contamination

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Subsurface contamination in both saturated and unsaturated soils is strongly dependent on the initial concentrations of pollutants at the source. We consider the problem of determining the location and rate of contamination in a saturated aquifer given samples of pressure and saturation data at various locations in the aquifer. We present a mathematical formulation which expresses the problem as the solution to an inverse problem.

INTRODUCTION

Contamination in the saturated and undersaturated subsurface soils is strongly dependent on the initial concentrations of pollutants at the source. In this paper, we consider the problem of locating the source of a contaminant and determining the rate of contamination given samples of pressure and saturation data at various locations in the aquifer.

We consider a forward model for two-phase flow (one of the phases being the contaminant). This model uses a standard formulation which describes the pressure and saturations in the aquifer as a function of sink and source terms and material properties. The objective of this paper is to reformulate the problem of locating the source of a contaminant and determining the rate of contamination as an inverse problem. In the process, we introduce some of the mathematical issues related to solving such inverse problem of the forward model.

A very challenging area of computational mathematical research today deals with solving inverse problems. Fundamental concepts of inverse theory have been developed for seismic inverse problems by Tarantola[1, 2, 3, 4]. Recently there has been a growing interest in applying inverse problem theory to reservoir characterization (see, for example, [5, 6, 7]). In this paper, we apply the theory to the problem of locating the source of a contaminant and determining the rate of contamination given samples of pressure and saturation data at various locations in the aquifer.

THE FORWARD MODEL

We consider a forward model which describes the pressure and saturations in the aquifer as a function of sink and source terms and material properties. This model uses a standard formulation of two-phase (one of the phases being the contaminant), immiscible, incompressible flow in a porous medium:

$$\Phi\frac{\partial S_w}{\partial t} - \nabla\cdot\left(k\frac{k_{rw}}{\mu_w}(\nabla p_w + \rho_w g\nabla z)\right) = \delta(x-x_w, y-y_w)Q_w \qquad (1)$$

$$\Phi\frac{\partial S_c}{\partial t} - \nabla\cdot\left(k\frac{k_{rc}}{\mu_c}(\nabla p_c + \rho_c g\nabla z)\right) = \delta(x-x_c, y-y_c)Q_c, \qquad (2)$$

where the subscripts w and c denote water and contaminant phases respectively. The equations (1)-(2) consider two source functions. Water enters the domain at location (x_w, y_w) at a rate Q_w, while a contaminant is produced at a rate Q_c at location (x_c, y_c).

In addition to the above equations we have

$$S_w + S_c = 1. \tag{3}$$

Let the capillary pressure between the contaminant and water phases be given by

$$p_{cw} = p_c - p_w. \tag{4}$$

Then, equations (1)–(4) can be rewritten as:

$$\Phi \frac{\partial S_w}{\partial t} - \nabla \cdot \left(k \frac{k_{rw}}{\mu_w} (\nabla p_c - \nabla p_{cw} + \rho_w g \nabla z) \right) = \delta(x - x_w, y - y_w) Q_w \tag{5}$$

$$-\Phi \frac{\partial S_w}{\partial t} - \nabla \cdot \left(k \frac{k_{rc}}{\mu_c} (\nabla p_c + \rho_c g \nabla z) \right) = \delta(x - x_c, y - y_c) Q_c. \tag{6}$$

THE DISCRETE MODEL

Equations (5)–(6) can be discretized using a semi-implicit discretization on a uniform cell-centered grid. In the following Δx and Δy refer to the uniform spacings in the $x-$ and $y-$directions, respectively:

$$\begin{aligned} \Delta x &= x_{i+1/2} - x_{i-1/2} = x_{i+1} - x_i = x_i - x_{i-1} \\ \Delta y &= y_{i+1/2} - y_{i-1/2} = y_{i+1} - y_i = y_i - y_{i-1} \end{aligned}$$

Where the finite difference operators Δ_x and Δ_y are defined by

$$\begin{aligned} [\Delta_x \cdot (T \Delta_x V)]_{ij} &= T_{i+1/2,j}(V_{i+1,j} - V_{i.j}) - T_{i-1/2,j}(V_{i.j} - V_{i-1,j}) \\ [\Delta_y \cdot (T \Delta_y V)]_{ij} &= T_{i,j+1/2}(V_{i,j+1} - V_{i.j}) - T_{i,j-1/2}(V_{i.j} - V_{i,j-1}). \end{aligned}$$

We also define

$$\Delta t^n = t^{n+1} - t^n \text{ and } \Delta s_w^{n+1} = s_w^{n+1} - s_w^n.$$

The relative permeabilities k_{rw} and k_{rc} are functions of the saturation S_w. Approximate k_{rw}^{n+1} and k_{rc}^{n+1} as

$$k_{rw}^{n+1} \simeq k_{rw}^n(S_w) + \left(\frac{dk_{rw}}{dS_w} \right)^n \Delta S_w^{n+1} \tag{7}$$

$$k_{rc}^{n+1} \simeq k_{rc}^n(S_w) + \left(\frac{dk_{rc}}{dS_w} \right)^n \Delta S_w^{n+1}. \tag{8}$$

The capillary pressure is approximated analogously:

$$p_{cw}^{n+1}(S_w) \simeq p_{cw}^{n}(S_w) + \left(\frac{dP_{cw}}{dS_w}\right)^n \Delta S_w^{n+1}. \tag{9}$$

Using equations (7) and (9) and the approximations $\Delta S_w^{n+1}\Delta_x p_c^{n+1} \simeq \Delta S_w^{n+1}\Delta_x p_c^n$ and $\Delta S_w^{n+1}\Delta_y p_c^{n+1} \simeq \Delta S_w^{n+1}\Delta_y p_c^n$ (and neglecting the product $\Delta S_w^{n+1}\Delta S_w^{n+1}$) equation (5) can be discretized as:

$$\begin{aligned}
&-\frac{\Delta y}{\Delta x}\Delta_x \cdot \left[\left(\frac{k}{\mu_w}\right)^n \left\{k_{rw}^n \Delta_x p_c^{n+1} + \left(\frac{dk_{rw}}{dS_w}\right)^n \Delta S_w^{n+1}\Delta_x p_c^n \right.\right. \\
&\qquad \left.\left. -k_{rw}^n \Delta_x \left(\left(\frac{dp_c}{dS_w}\right)^n \Delta S_w^{n+1}\right) + \left(\frac{dk_{rw}}{dS_w}\right)^n \Delta S_w^{n+1}\rho_w g \Delta_x z\right\}\right]_{ij} \\
&-\frac{\Delta x}{\Delta y}\Delta_y \cdot \left[\left(\frac{k}{\mu_w}\right)^n \left\{k_{rc}^n \Delta_y p_c^{n+1} + \left(\frac{dk_{rc}}{dS_w}\right)^n \Delta S_w^{n+1}\Delta_y p_c^n \right.\right. \\
&\qquad \left.\left. -k_{rc}^n \Delta_y \left(\left(\frac{dp_c}{dS_w}\right)^n \Delta S_w^{n+1}\right) + \left(\frac{dk_{rc}}{dS_w}\right)^n \Delta S_w^{n+1}\rho_w g \Delta_y z\right\}\right]_{ij} \\
&+\frac{\Delta x \Delta y \Phi}{\Delta t^n}(\Delta S^{n+1})_{ij} \\
= \;& \Delta x \Delta y \delta(x_i - x_w, y_j - y_w)(Q_w^{n+1})_{ij} \\
&-\frac{\Delta y}{\Delta x}\Delta_x \cdot \left[\left(\frac{k}{\mu_w}\right)^n k_{rw}^n \left(\Delta_x p_{cw}^n - \rho_w g \Delta_x z\right)\right]_{ij} \\
&-\frac{\Delta x}{\Delta y}\Delta_y \cdot \left[\left(\frac{k}{\mu_w}\right)^n k_{rw}^n \left(\Delta_y p_{cw}^n - \rho_w g \Delta_y z\right)\right]_{ij}.
\end{aligned} \tag{10}$$

Equation (6) is discretized in a similar fashion.

Turning our attention to the source rates, let Q_T be the total rate. Then Q_w^{n+1} and Q_c^{n+1} are approximated by

$$Q_w^{n+1} = \frac{Q_T\left[\left(\frac{k_{rw}}{\mu_w}\right)^n + \left(\frac{1}{\mu_w}\frac{dk_{rw}}{dS_w}\right)^n \Delta S_w^{n+1}\right]}{\left(\frac{k_{rc}}{\mu_c}\right)^n + \left(\frac{k_{rw}}{\mu_w}\right)^n} \tag{11}$$

and

$$Q_c^{n+1} = \frac{Q_T\left[\left(\frac{k_{rc}}{\mu_c}\right)^n + \left(\frac{1}{\mu_c}\frac{dk_{rc}}{dS_w}\right)^n \Delta S_w^{n+1}\right]}{\left(\frac{k_{rc}}{\mu_c}\right)^n + \left(\frac{k_{rw}}{\mu_w}\right)^n}. \tag{12}$$

Combining equation (10) with the discretization of equation (6) and equations (11) and (12) yields a system of linear equations

$$Au = f, \tag{13}$$

where

$$\begin{aligned} A &\equiv A(p_c^n) \text{ is a function of } p_c^n \\ u &\equiv u(p_c^{n+1}, \Delta S_w^{n+1}) \text{ is a function of } p_c^{n+1} \text{ and } \Delta S_w^{n+1} \\ f &\equiv f(x_w, y_w, x_c, y_c, Q_T, p_c^n). \end{aligned}$$

This equations represent the forward model where the pressure and saturations are determined from initial conditions and source terms.

THE INVERSE MODEL

We now develop an inverse model to solve the original problem. We apply a maximum *a posteriori* estimator to develop the inverse model. Assume that the model parameters x_c, y_c and Q_T are all independent of time. If we know the source rate of the water phase and the total flow rate, then we can determine the source rate of the contaminant phase by subtraction.

Let $m = [x_c, y_c, Q_T]^T$ be the vector of model parameters and d the vector of observed or measured data. If we assume that the data is a linear function of the parameter m (which, of course, is not the case), then

$$d_{obs} = g(m) + \epsilon \tag{14}$$

where ϵ is an error vector [1].

If m_{prior} is our prior information on the model parameters, then the most probable model minimizes

$$S(m) = \frac{1}{2}\left[(m - m_{prior})^T C_M^{-1}(m - m_{prior}) + (g(m) - d_{obs})^T C_D^{-1}(g(m) - d_{obs})\right] \tag{15}$$

where C_D is the covariance matrix for the measurement errors and C_M is the covariance matrix for the model parameters [1]. C_D is diagonal since the components of the measurement error vector ϵ are assumed to be independent.

The Gauss-Newton method can be used to find the minimum of $S(m)$. For this, we need the gradient $\nabla S(m)$ of S at m and the Hessian matrix

$H(m)$. They are given by

$$\nabla S(m) = G^T C_D^{-1}(g(m) - d_{obs}) + C_m^{-1}(m - m_{prior}) \quad (16)$$

$$H(m) = G^T C_D^{-1} G + C_M^{-1}, \quad (17)$$

where G is the sensitivity matrix [1].

Let N be the number of grid blocks, N_t be the number of measurements made, and N_{obs} be the number of grid blocks where measurements are taken. Then

$$\begin{aligned} C_M &\quad \text{is a } 3 \times 3 \text{ matrix} \\ N_d = 2N_{obs} \cdot N_t &\quad \text{is the number of observed data} \\ C_D &\quad \text{is an } N_d \times N_d \text{ matrix} \\ G &\quad \text{is an } N_d \times 3 \text{ matrix} \end{aligned}$$

and G has the form:

$$G = \begin{bmatrix} G_1 \\ G_2 \\ . \\ . \\ . \\ G_{N_t} \end{bmatrix}.$$

If we order the unknowns corresponding to the N_{obs} grid blocks where measurements are taken as:

$$(p_c^n)_{i_1 j_1}, (\Delta S_w^n)_{i_1 j_1}, \cdots (p_c^n)_{i_{N_{obs}} j_{N_{obs}}}, (\Delta S_w^n)_{i_{N_{obs}} j_{N_{obs}}}$$

then the sensitivity matrix G_n at the $n-$th measurement is:

$$G_n = \begin{bmatrix} \left(\frac{\partial p_c^n}{\partial x_c}\right)_{i_1 j_1} & \left(\frac{\partial p_c^n}{\partial y_c}\right)_{i_1 j_1} & \left(\frac{\partial p_c^n}{\partial Q_T}\right)_{i_1 j_1} \\ \left(\frac{\partial \Delta S_w^n}{\partial x_c}\right)_{i_1 j_1} & \left(\frac{\partial \Delta S_w^n}{\partial y_c}\right)_{i_1 j_1} & \left(\frac{\partial \Delta S_w^n}{\partial Q_T}\right)_{i_1 j_1} \\ . & . & . \\ . & . & . \\ . & . & . \\ \left(\frac{\partial p_c^n}{\partial x_c}\right)_{i_{Nobs} j_{Nobs}} & \left(\frac{\partial p_c^n}{\partial y_c}\right)_{i_{Nobs} j_{Nobs}} & \left(\frac{\partial p_c^n}{\partial Q_T}\right)_{i_{Nobs} j_{Nobs}} \\ \left(\frac{\partial \Delta S_w^n}{\partial x_c}\right)_{i_{Nobs} j_{Nobs}} & \left(\frac{\partial \Delta S_w^n}{\partial y_c}\right)_{i_{Nobs} j_{Nobs}} & \left(\frac{\partial \Delta S_w^n}{\partial Q_T}\right)_{i_{Nobs} j_{Nobs}} \end{bmatrix}$$

The Gauss-Newton iterations updates for the model parameters are:

$$m^{l+1} = m^l - \left[H(m^l)\right]^{-1} \nabla S(m^l)$$

where

$$\begin{aligned} H(m^l) &= G^T C_D^{-1} G + C_M^{-1} \\ \nabla S(m^l) &= G^T C_D^{-1}(g(m^l) - d_{obs}) + C_M^{-1}(m^l - m_{prior}). \end{aligned}$$

CALCULATING THE SENSITIVITY MATRIX

In the preceding section, it has been shown that one of the critical issues for an estimation of the inverse problem is the calculation of the sensitivity matrix G. There are several methods proposed in the literature to calculate a matrix of partial derivatives such as this. Some authors use finite difference methods to calculate the derivatives. This method is sensitive to truncation and round-off errors and it is not recommended.

There are at least two other interesting approaches for handling the calculation of G. One method is computational differentiation. Computational differentiation techniques are applied to the code that produces the pressures and saturations to generate code that can compute the desired derivatives [8]. The other approach is to evaluate not the matrix G. but its action on a given vector. In recent work, Chu et. al. [7], derive an algebraic relationship between the input parameters and the pressures and saturations using matrix representations of the finite difference equations. The generation of the sensitivity matrix is done implicitly using matrix-vector multiplies. The matrix-vector multiplies requires at each time step the solution of a system of linear equations.

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Treatment of Produced Water and Wastewater

A NOVEL TREATMENT MATERIAL FOR REMEDIATING ORGANIC METALLIC, AND RADIONUCLIDE CONTAMINANTS IN THE PRODUCED WATERS FROM THE OIL AND GAS INDUSTRY

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ABSTRACT

The National Pollution Discharge Elimination System (NPDES) of the Clean Water Act (Section 402, 23 USC) requires a zero discharge limit for the grease and oil contained in the produced waters from the Gulf Coastal Region of Texas and Louisiana. Produced water is usually contaminated with metals, BTEX VOCs and other chemicals that might pose a threat, if discharged without treatment, to the marine and terrestrial biomes along the coastal region. A new adsorbent material, HUMASORB™, developed by ARCTECH has the potential to remove both organics and metal ions as well as the radionuclides from the produced water in a single process step. This paper describes the work conducted as part of the development of HUMASORB™ Technology to remove target contaminants from the simulated contaminated water streams.

INTRODUCTION

During exploration and production (E&P) operations of oil and gas, three types of wastes are generated: drilling wastes, "other" associated wastes and the produced water. Produced water is the water generated with the product stream containing oil and/or natural gas. This water must be separated from the product stream before the sale of oil or gas. Depending upon the source[10,11,24], the produced water, contains organics (volatile organics [VOCs] and volatile fatty acids [VFA]), anions (Cl^-, HCO_3^-, SO_4^{-2}, SO_3^{-2} to name a few), ammoniacal nitrogen, metals (eg. antimony, arsenic, barium, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, silver, strontium, thallium, zinc etc.) and radionuclides (total concentration 19-2,800 picocuries/l). Produced water must be treated and disposed off in an environmentally safe manner. The major environmental regulations governing the treatment and disposal of the produced water are the:

- Resource Recovery and Conservation Act (RCRA),
- Clean Water Act (CWA), and
- Safe Drinking Water Act (SDWA)

A. Overview of Regulations, Remediation Technologies for Produced Water and Associated Cost of Remediation

The state-of-the-art technology to comply with these regulations is Dissolved Gas Flotation[12]. This method, however, is not sufficient to comply with the ever increasing stringent environmental regulations. In order to better understand this problem, the available solutions and fully appreciate the necessity for a cost-effective, operator-friendly and environmentally benign technology, it is worthwhile to review:

- regulatory requirements,
- the chronology of the standards promulgated under these regulations,
- discuss the potential technologies to comply with the standards, and
- associated costs based on current technologies and regulations as well as the projected costs to comply with newly promulgated regulations.

1. Regulatory Requirements

In the interest of protecting public health and welfare, the Water Quality Improvement Act of 1970 (P.L 91.224) prohibits the discharge of oil into the territorial waters of the U.S. Subsequently promulgated rules prohibit the discharge of oily wastes that would be sufficient to create a film, sheen, or discoloration of the U.S. coastal waters or the adjoining shorelines, or causes a sludge or emulsion to be deposited underneath the water surface[8].

In 1976, the RCRA was promulgated to manage the solid and hazardous wastes and to promote waste reduction through recycling[10]. Two sections, Subtitles C and D of RCRA are pertinent to the oil and Gas E&P operations. Subtitle C addresses management, transport, treatment and disposal of the hazardous wastes. Under RCRA, a waste stream is defined/listed to be hazardous on the bases of its ignitability, corrosivity, reactivity or toxicity to humans, wild life and plant. RCRA Subtitle D, on the other hand, provides federal guidance whereby the states regulate the non-hazardous wastes.

In 1980, subject to further review from the Environmental Protection Agency (EPA), the United States Congress exempted the wastes associated with the Oil and Gas Industry E&P operations from categorization as a hazardous waste according to the RCRA Subtitle C. A 1987 report from the EPA justified the exemption. The justification was made on the basis of large volumes and comparatively low toxicity of the wastes associated with Oil and Gas E&P operations. Subsequently, a 1988 regulatory determination by the EPA confirmed the justification that EPA made in 1987. Consequently, at the present time, except for the drilling wastes and produced waters, all other oil and Gas E&P operations wastes are not subject to RCRA subtitle C, they are, however, regulated by the RCRA Subtitle D regulations.

Produced water must be treated and disposed off according to RCRA Subtitle C, the Safe Drinking Water Act (SDWA), or the Clean Water ACT (CWA). Following methods are prevalent in the industry for the environmentally friendly disposal of produced waters[11].

- subsurface injection/reinjection,
- surface discharge to the coastal and non-coastal areas, and
- offshore discharges.

The subsurface reinjection of the produced water is regulated under Section 1422 of the SDWA. According to this subsection all underground injection of the produced waters should be in accordance with

the Underground Injection Program (UIP). These programs are either run directly by the EPA or some States have retained the primary rights to enforce UIP under the auspices of the EPA.

On the other hand, under the authority of CWA (subsection 402, 33 USC 1342), produced water discharge to most of the coastal or surface areas are state-regulated and have to comply with the following:

1. discharges to the coastal areas that contain brackish water unsuitable for human usage (relevant for California, Louisiana and Texas),
2. discharge consists of low salinity that are useful for irrigation or livestock watering in arid zones west of 98th meridian (primarily Wyoming),
3. discharges are from stripper wells, stripper wells are the wells that produce <10 bbl/day oil but yield up to 100 bbl water for each bbl of oil produced.

Nevertheless, the Road and Land spreading methods of surface discharge are governed by both CWA (subsection 402, 33 USC 1342) and RCRA, Subtitle C. At the same time offshore produced water disposal practices are regulated primarily under the authority of SDWA, CWA and in case of road spreading by RCRA Subtitle C. In most of the regions these regulations are carried out and monitored by either the EPA, or the State Environmental Statutes under the authority of the EPA. These regulations also apply to offshore-platform produced water as well as those produced in California, Louisiana and Texas. In Louisiana, the Louisiana Department of Environmental Quality (LDEQ) and in Texas, the Railroad Commission (TRRC) has the jurisdiction over, and the responsibility to carry out these regulations.

On the basis of different industry and EPA sponsored surveys, the rule of 72/48 mg/l was established prior to 1993[10,14]. The 72 mg/l being the monthly maximum and 48 mg/l being the monthly average limit. In 1994, the EPA promulgated new 42/29 mg/l standards. The Offshore Operations Committee commissioned a study to survey the water treating systems currently operating in the Gulf of Mexico. The results of the survey show that nearly 60% of the operating platforms were not able to comply with the new regulatory standards[14,15]. Simultaneously, for the coastal regions of Louisiana and Texas a new standard of zero discharge was announced in the Federal register of January 9, 1995 which is effective as of February 8, 1995[24]. This announcement is based on the potential threat to terrestrial flora and fauna in the coastal Gulf of Mexico. The rule is applicable to the Coastal subcategory, which is any body of water landward of the territorial seas or wetland adjacent to such waters.

2. *Volumes of Produced Water from Oil E&P Operations*

The magnitude of the problem and the cost facing the oil industry can easily be realized from the data on the quantities of produced water[3,7] generated from different sources as summarized in Table 1. The problem is further enhanced[7] because as the wells mature, the ratio of water to oil increases. Stripper wells (producing < 10 barrels (bbl)/day) can yield up to 100 bbl water/ bbl oil. The severity of the compounded problem is further realized based on the fact that a 29% increase in the stripper wells is reported for the period 1970 to 1990. In the Gulf Coast Region (Texas[TX], Louisiana [LA]), produced water is the largest waste stream, although Oklahoma (OK) and Wyoming (WY) also produce large quantities of produced water During 1995, >254 MMbbls of produced water were discharged to surface waters in both Texas and Louisiana. This has been the widely used disposal method in the Gulf Coast Region. There are three conventional ways of discharging the produced water:

1. reinjection into the formation/wells,

2. evaporation and percolation, and
3. road or land spreading.

In regions such as Wyoming, about 90% of the water is re-injected into the underground formation. Of the 90%, 30% is injected in to the disposal wells while the rest is used in the enhanced oil recovery operations. The remaining water is disposed off through evaporation, percolation and road spreading.

3. State-of-the-Art Technologies to Comply with Regulations

Two technologies have been used for the industry-wide usage. These technologies have taken in to consideration the regulatory as well as space constraints associated with offshore platform operations[10,14,15]. These include the hydrocyclone and the cross-flow membrane filtration. The drivers behind the development and application of these technologies are the stringent regulations and unique needs pertaining to North Sea Operations.

HYDROCYCLONE The basic principle of the hydrocyclone operation is that the oil and grease particles separate from the produced water by the centrifugal force affected by a swirling flow pattern and differences in the density of water and the oil/grease. There are two types of hydrocyclones:

- the static model that effectuates separation by the swirling pattern created through the surge of produced water at a high pressure,
- the rotary model provides the same effect through mechanical rotation to generate a vortex.

Thus, the oil droplets grow in size from ~ 100m to 1000m. The less dense oil droplets move toward the center and back to the separator. By using a coalesce upstream of the hydrocyclone a 10-15% enhancement in the oil removal efficiency can be obtained. The major reason for the limited commercial usage of this technology are:

- high capital cost ($40,000 to $750,000) in comparison to conventional technology, such as gas floatation,
- can not remove oil and grease below the 15-25 mg/l range.

CROSS-FLOW-MEMBRANE FILTRATION This is the most effective technology to remove the produced water from the production stream. The produced water is directed parallel to the membrane surface, the force of the flow allows the clean water to pass through the membrane, while the oil and grease contents are concentrated. The concentrate can then be recycled through the system. This technique prevents the contaminants from coming in direct contact with the membrane. Thus saving the membrane surface from clogging. The pore size of the membrane range from 0.03m to 0.8m. The membranes can be constructed from a variety of materials such as cellulose, polyphosphone, alumina, and stainless steel etc. The operating costs[7] vary from $0.02 to $0.03/ bbl at the inlet volume of 10,000 bbl/day (BWPD) in contrast to conventional treatment (gas flotation system) operating cost of $0.01/bbl. The installed cost for a 10,000 BWPD is ~$1.4 million. Therefore, the limiting factors prohibiting generalized usage of the Cross-flow membranes are:

- capital cost ($1.4 million as against $400,000 for the gas flotation system (conventional technology) processing 10,000 BWPD),

- clogging of the membranes (membrane fouling), and
- sensitivity to disruptions in the pH levels of the influent.

4. Associated Costs

The American Petroleum Institute (API) estimates that in 1990 the cost to comply with then existent environmental regulations was around $1.5 billion for the E&P segments and $6.3 billion for the entire oil and gas industry[2]. This translates to a cost of $13.5 to $120.8 billion with the new regulations promulgated[9] during 1995. The ICFR has estimated an annual incremental cost of $1.4 to $8.1 billion due to new regulations. The API[3], however, estimates that the initial cost for compliance with the zero discharge guidelines is $289 million for coastal areas and $3.223 billion for offshore areas. Estimated annual operating costs range between $23 million to $270 million.

B. Potential Technologies to Comply with New Newly Promulgated Regulations

These limitations of the current technologies have spurred the interest of the industry to evaluate some of the technologies from other industries[10] for the treatment of produced water. Nevertheless, as indicated in Table 2, none of these materials or technologies have the capability of removing all the contaminants of the produced water in one step. Moreover, the R&D costs of such attempts is enormous. The following section provides some of the costs related to the treatment of the produced waters.

Thus, from the foregoing discussion on the regulatory requirements, available technologies to comply with such requirements and the estimated costs, it is apparent that the Oil and Gas E&P operations industry needs a cost-effective, environmentally benign and operator friendly technology to treat the produced water. The data presented in this paper, show that the HUMASORB™ product is potentially applicable for a single step, cost effective, remediation system for the mitigation of organics, metals and the radionuclides from the produced waters including the wastewaters from the oil and gas production sites. The other requirements of the oil and Gas E&P and operations are at the offshore sites where besides the environmental regulations, additional constraint of limited space has also to be met. HUMASORB™column being a vertical, rather than horizontal operation meets that requirement.

Overview Of HUMASORB™ Technology

HUMASORB™ (Patent pending) line of products are humic acid based adsorbent derived from *actosol*®, an organic soil conditioner/ fertilizer manufactured and sold by ARCTECH in national and international markets. HUMASORB-S™ is a solid form of HUMASORB-L™, whereas HUMASORB-CS™ is a cross-linked, immobilized form of HUMASORB-L™/HUMASORB-S™ and incorporates the following properties of humic acid that are useful for remediation of contaminated streams:

- high cation exchange capacity,
- ability to chelate metals, and
- ability to adsorb organics

Brief Review of Humic Acid Properties

Humic acid is a dark brown to black colored complex organic macromolecule (Figure 1 shows the empirical structure) containing various functional groups. The molecular weight of this molecule varies from 1,000 to

300,000 daltons. This polyelectrolyte can be derived from coal, peat, humate and is the major ingredient of top soil or soil humus. Some of the other attributes of this molecule are:

1. high cation exchange capacity,
2. ability to chelate metals,
3. ability to adsorb organics,
4. coagulate easily with electrolytes, and
5. because of being organic is easily combustible.

Some of these attributes, such as chelation of radionuclides and heavy metals, of the humic acid have been reported in the literature[13,16]. Pahlman and Khalafalia[16] have established that the metal chelation capacity of humic acid from a number of sources that they tested is a function of the pH of the reaction medium. For complete removal of the metals a pH range of 6.5 to 9. 5 was determined to be optimal in their study.

Chiou[5] and Choudhary[6] have extensively studied the adsorption of organics by humic acids. The organic compounds studied include:

- non-ionic organics such as benzene, halogen substituted benzenes, and chlorinated hydrocarbons such as 1,1,1-trichloroethane (TCA),
- polychlorinated biphenyls (PCBs),
- nitrogen compounds, such as urea and anilines,
- fumigants (telone) and insecticides (DDT),
- herbicides, such as paraquat, diquat and triazines, and
- organophosphorus compounds such as parathion.

Chiou[5] attributes the adsorption of nonionic organics, such as benzene, halogen substituted benzenes and chlorinated hydrocarbons such as TCA, contained in water to primarily solute partitioning into the humic acid (organic sorbent). Choudhary[6], on the other hand, postulates that the mechanism for the adsorption of organic compounds could be due to any one or a combination of two or more of the following :

- Van der Waals attractions,
- hydrophobic bonding
- hydrogen bonding
- charge transfer,
- ion exchange, and
- ligand exchange.

The stable, free radicals in humic acid are believed to be playing a role in the adsorption of nitro-organics such as aniline and urea[17], perhaps due to the formation of an addition complex through the carboxyl and phenolic hydroxyl groups[6] in the humic acid (Figure 1). Adsorption of PCBs from the aqueous streams is, however, attributed to a number of functional groups present on the humic acid molecule. This is based on a linear increase in the adsorption of PCBs to humic acid[8] as a function of increase in Cl^{-1} in the PCB arochlors and the fact that the adsorption isotherms followed the Freundlich equation where the constant K (measure of the adsorptive capacity) increased from di- to hexa-chloro PCB, i.e. from lower to higher PCB arochlors[18].

From the discussion on the properties of humic acid, it is clear that humic acid could potentially be the material of choice to remove the target metals and organics from the produced water streams. The basic drawback, however, is that humic acid complex is water soluble at pHs ≥2, especially in the presence of some monovalent ions such as K^{+1} and Na^{+1}. The HUMASORB™ product developed at ARCTECH overcomes this problem because through a unique proprietary technology, the HUMASORB™ is water insoluble at pHs of up to 12 and sparingly soluble at pHs > 12.

MATERIALS AND METHODS

The materials and methods used to prepare HUMASORB™ and the procedures to evaluate its properties, as well as the analytical methods are detailed elsewhere[18].

RESULTS AND DISCUSSION

HUMASORB-S™ and HUMASORB-CS™ showed fairly good removal of each of the three major class of contaminants, viz. metals, radionuclides and organics, commonly encountered in the produced water (Table 3). Therefore, these are an ideal material for the single step treatment of the.produced water.

Properties of HUMASORB-S™ and HUMASORB-CS™

The purified *actosol* ®humic acid (HUMASORB-S™) and those encountered in the literature are water soluble[5,8,, 13,16-18] at pH>2 (Figure 2). HUMASORB-CS™, whether prepared chemically or enzymatically remains insoluble in water up to a pH of ~7. Further preparation, makes the HUMASORB-CS™ insoluble up to a pH of 12 (Figure 2). Thus prepared HUMASORB™ not only retains the original properties of humic acid, but also enhances the contaminant removal capacity of this product (Figures 3-8) in contrast to both humic acid as well as HUMASORB-S™.

Metals Removal

HUMASORB-CS™ was produced by cross-linking and immobilization of HUMASORB-L/S™ using different proprietary methods. The solubility of the cross-linked product was determined at various pH levels and compared with humic acid. The results in Figure 2 show that the solubility of HUMASORB-CS™, as determined under the conditions of this study, is significantly lower compared to that of humic acid. The different functional groups present in HUMASORB™ before and after cross-linking were estimated using ^{13}C-NMR. The analysis indicates that all the functional groups are retained after cross-linking

The ability of HUMASORB-CS™ to remove different contaminants was evaluated and compared with removal before cross-linking. The results from simulated streams containing single contaminants such as chromium (Figure 3), strontium (Figure 4) and streams containing multiple contaminants such as copper, chromium and lead (Figures 5 and 6), or organics (figure 8) indicate that contaminant removal is retained and, in a few cases, enhanced after cross-linking. In addition, the results using a mixed metal stream indicate that chromium removal is the rate limiting step and required a higher loading of the adsorbent (Figure 3). This finding is similar to the performance of HUMASORB™ before cross-linking (Figure 5).

Furthermore, the removal of these metals and those typically present in the produced waters (Table 3) follow the Langmuir (data not presented) and Freundlich models [8,18] as illustrated by the examples of copper and nickel (Figure 7). Further analysis of the adsorption isotherms of these metals on the HUMASORB™ indicates that the metal removal by HUMASORB™ also fits the Scatchard equation[19]. This equation shows that the number of inflection points on a Scatchard plot (figure 9) indicate the number of the binding sites on the adsorbent. On this basis, in case of nickel and copper , there are at least 2 binding sites for copper (Figure 9) and possibly three for nickel. Thus, HUMASORB-CS™ is applicable for the removal of metals commonly found in the produced water (Table 4).

These studies also indicate that the chromium III removal is HUMASORB™ mediated and is not only a function of pH of the water (Figure 10). This data is in agreement with the Bureau of Mines studies on humic acid[16]. In contrast to the data presented by Pahlman and Khalafalia[16], however, the data on HUMASORB™ mediated chromium removal shows that highly toxic chromium (VI), representing an oxy-ion in the form of potassium dichromate ($K_2Cr_2O_7$) first gets reduced to less toxic chromium (III) and then chromium (III) is consistently removed (Figure 11) from the contaminated water stream. This data is also in agreement with those reported by a number of other authors for iron, mercury, plutonium and vanadium[1,4 , 22, 23]. Furthermore, the increase in the loading of the adsorbent (HUMASORB-S™ or HUMASORB-CS™) enhances the removal rate of chromium (Figure 3), which is another indication that the chromium removal is not a function of pH alone. The efficacy of HUMASORB™ in removing the metallic contaminants from the wastewaters is further confirmed by the rates of removal of metals from a waste water stream obtained from a superfund site (Table 5). These data clearly indicate that the contaminnats present in the produced water (Table 3) can be effectively removed by the HUMASORB-CS™ (Table 4).

The results from various experiments conducted using different forms of HUMASORB™ are tabulated in Table 5. These results were used to determine the distribution coefficient, Kd, defined as:

$$K_d \equiv C_s / C_l$$

where,

C_s is the concentration of the contaminant in the solid phase

and C_l is the concentration in the liquid phase.

The distribution coefficients for various contaminants are listed in Tables 6-7. The values were determined from batch isotherm studies in which different amounts of the adsorbent were contacted with simulated waste streams. The data presented in these tables further strengthen the efficiency of HUMASORB™ products to remove the metallic contaminants from the produced water. Moreover, these data also indicate that the distribution coefficients for any given metal were much higher with the HUMASORB-CS™ than HUMASORB-S™ at comparatively lower equilibrium concentrations. This means that HUMASORB-CS ™ enhances the contaminants removal from the produced water.

Removal of Radionuclides

The removal pattern(Figures 4 and 6) for the radionuclides represented by cerium (as surrogate of plutonium) and strontium showed results similar to those of non-radioactive metals. These data provide sufficient evidence that HUMASORB-CS™ can remove radionuclides in produced waters. Further evidence for the efficient removal of radionuclides by the HUMASORB™ products comes from the distribution coefficients of different radionuclides (Table 6). These data indicate that uranium has a very high affinity for HUMASORB-S and that HUMASORB-CS

has even higher affinity for the same radionuclide. Depending upon the radionuclide this enhancement can be 4 to 10 fold higher (Table 7)

Removal of Organics

Organics removal by the HUMASORB™ products show higher removal of polar organics, such as chlorinated hydrocarbons (eg. TCE) than the non-polar organics (Figure 8). Similar to the pattern observed with the metals removal, the removal of test organics enhanced with the HUMASORB™ loading (Figure 8). The Langmuir and Freundlich isotherms of the adsorption of TCE, PCE and benzene by HUMASORB™ are also indicative of the polar and the non-polar characteristics of the chlorinated and non-chlorinated organics. While isotherms of benzene and PCE adsorption completely followed both the models (Figure 11), those on TCE did not fit either the Freundlich or the Langmuir equations (Figure 12). The isotherms on TCE adsorption shows two distinctive phases: one up to 210 ppm and other showing rapid adsorption beyond 210 ppm. Even though, the PCE adsorption followed both the isotherms, the values for Langmuir model for this contaminant gave negative values (Table 8).

CONCLUSIONS

The experimental data presented in this paper on the removal of metallic as well as organic contaminants from both spiked water and the actual water obtained from a superfund site prove beyond doubt that HUMASORB™ products are a novel material that have the potential for removing all the contaminants from the produced water in a single step. The data also suggest that toxic metals present as oxy-anions are reduced to less toxic state. The HUMASORB-S™ can be cross-linked and immobilized which provides enhanced removal capabilities to the HUMASORB-CS™ product.

ACKNOWLEDGMENTS

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Table 1: Quantities of Produced Water Generated During E & P Operations

Location	Total Production (in Billions of Barrels, BB) of		Ratio of Oil:Water
	Oil	Water	
Onshore	2.05	14.00	1:7
Offshore[3]	0.22	0.90	1:4

Table 2: Among the Technologies HUMASORB™ Offers a Single Step Remediation for All the Contaminants Present in the Produced Waters

REMEDIATION TECHNOLOGY

	REMOVES METALS	REMOVES RADIONUCLIDES	REMOVES OXO-ANIONS	REMOVES ORGANICS
HUMASORB-L™	YES	YES	YES	YES
HUMASORB-CS™	YES	YES	YES	LOW
Gas Flotation	NO	NO	NO	YES
Coalescers	NO	NO	NO	YES
Skim Tank	NO	NO	NO	YES
Cation-Exchange	YES	YES	NO	NO
Anion-Exchange Resin	NO	NO	YES	NO
Chemical Precipitation	YES	YES	NO	NO
Reverse Osmosis	YES	YES	NO	NO
Polymer Filtration	YES	YES	NO	NO
Freeze Crystallization	YES	YES	Not Clear	NO
Coagulation/Flocculation	YES	YES	NO	NO
Chemical Oxidation	YES	YES	NO	YES
AMBERSORB™	NO	NO	NO	YES
Activated Carbon	NO	NO	NO	YES
Photolysis	NO	NO	NO	YES
Media Filtration	NO	NO	NO	YES
Air/Steam Stripping	NO	NO	NO	YES
Distiullation	NO	NO	NO	YES
Sonic Treatmnet	NO	NO	NO	YES
Biological Reactors	NO	NO	NO	YES

Figure 1: The Empirical Structure of Humic Acid

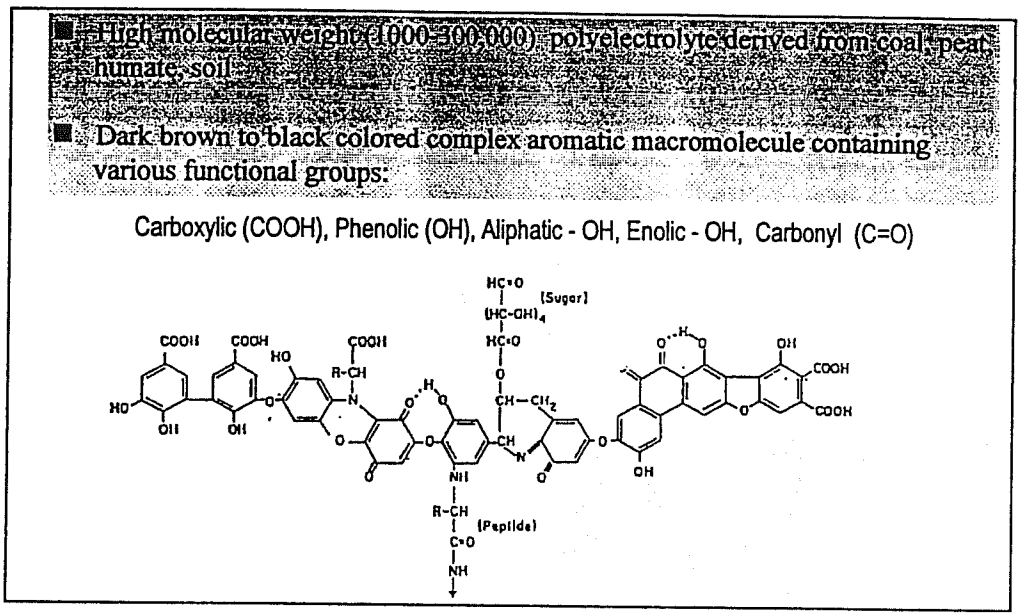


Figure 2: Solubility of HUMASORB-CS™ is Lower After Immobilization

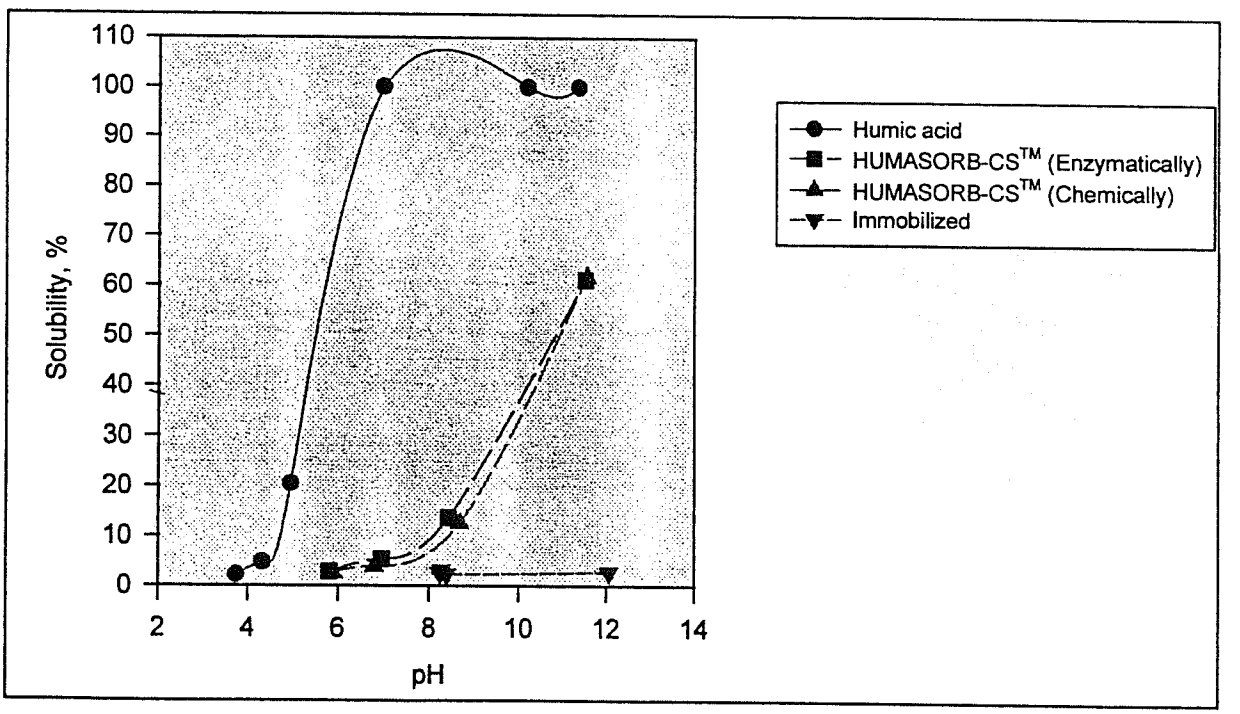


Figure 3: Chromium Removal is Significantly Enhanced with HUMASORB-CS™

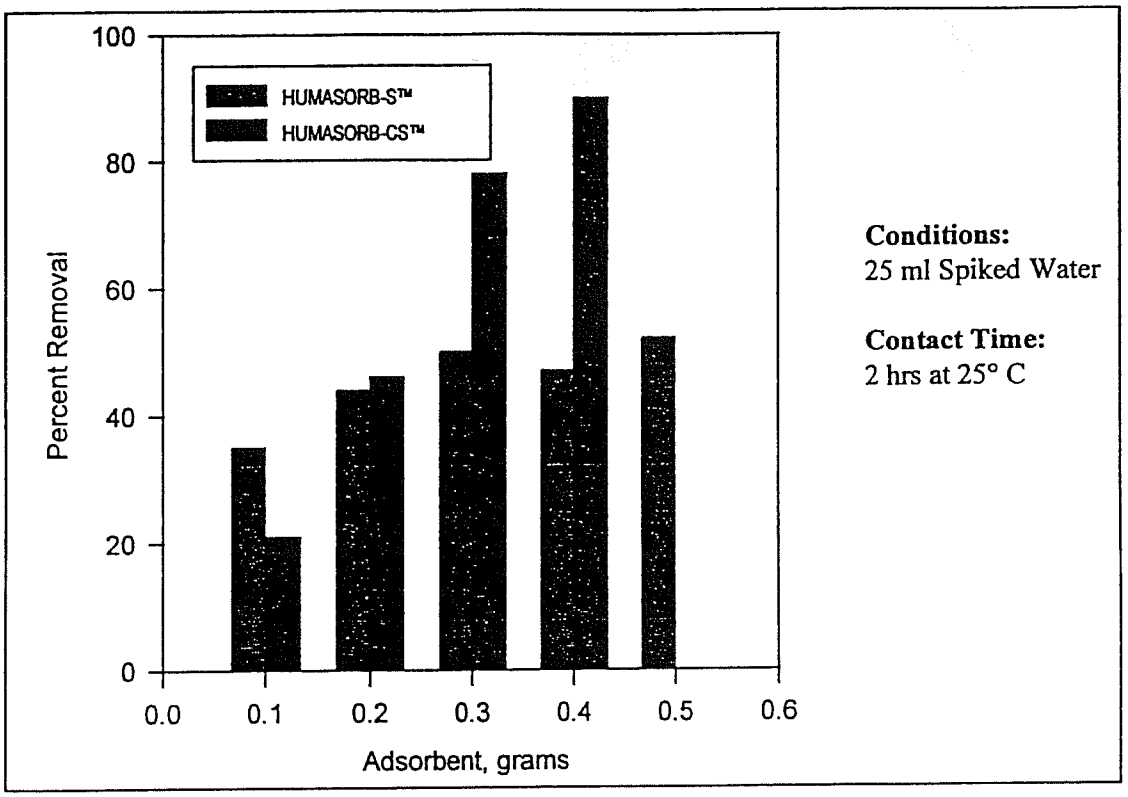


Figure 4: HUMASORB-CS™ Enhances Strontium Removal

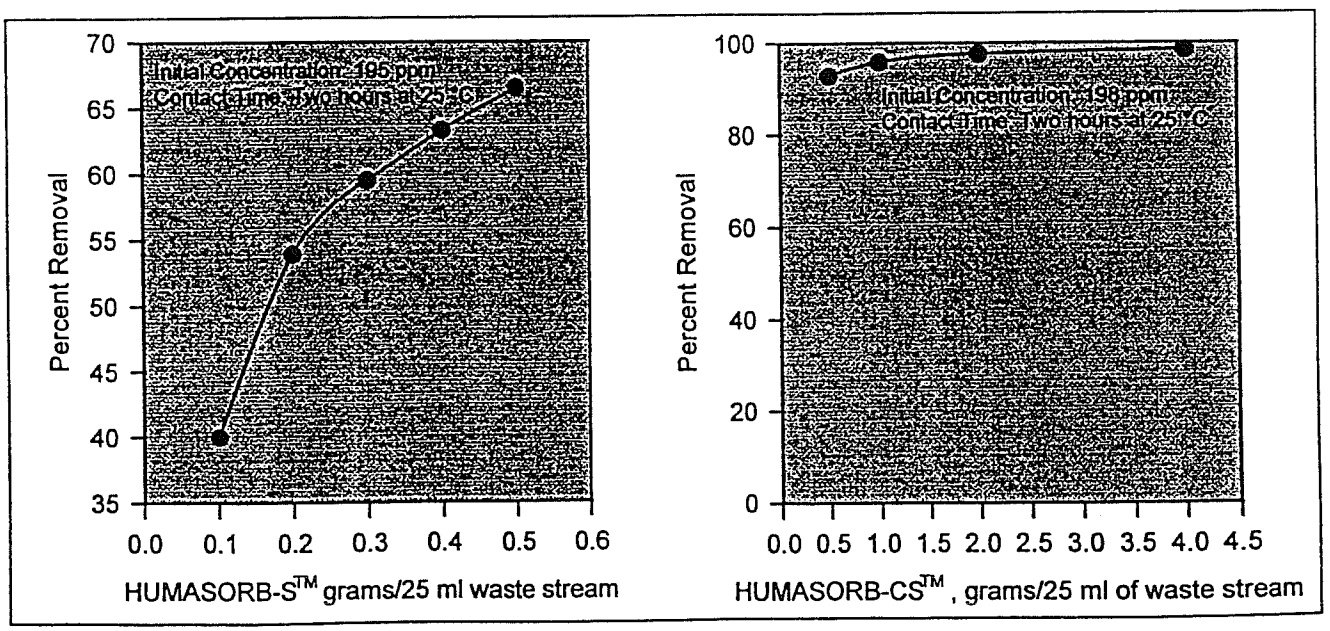


Figure 5: Mixtures of Metals are Removed and Remain Bound to HUMASORB-S™

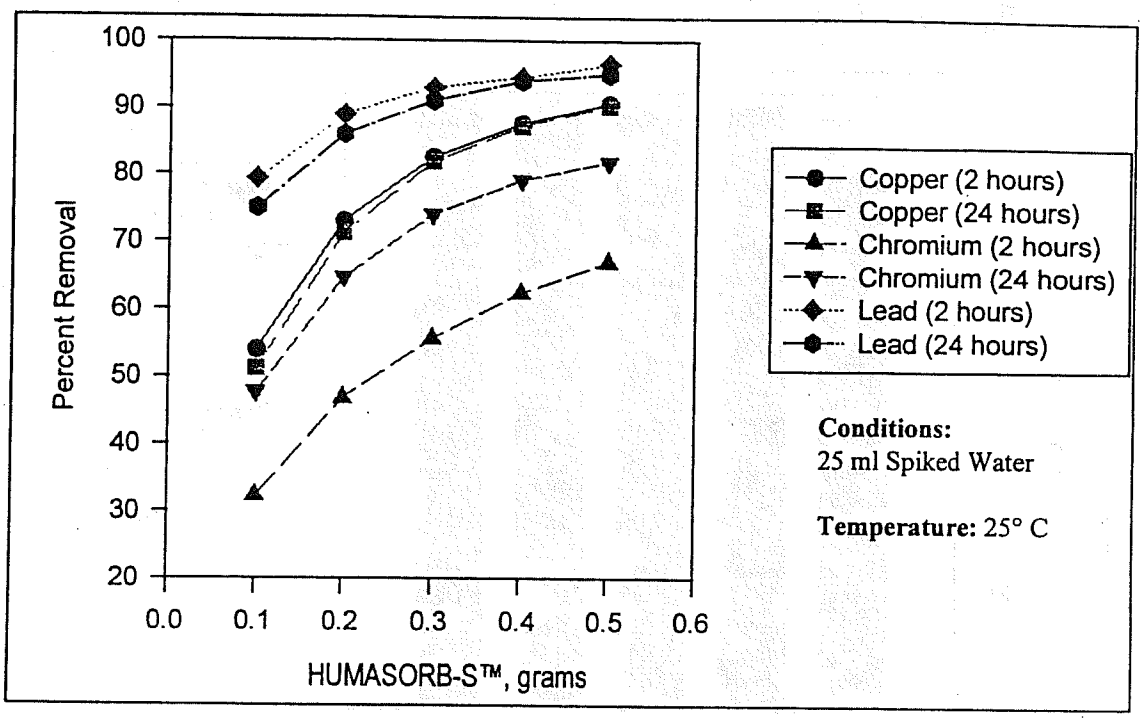


Table 3: The Contaminants in Produced Water

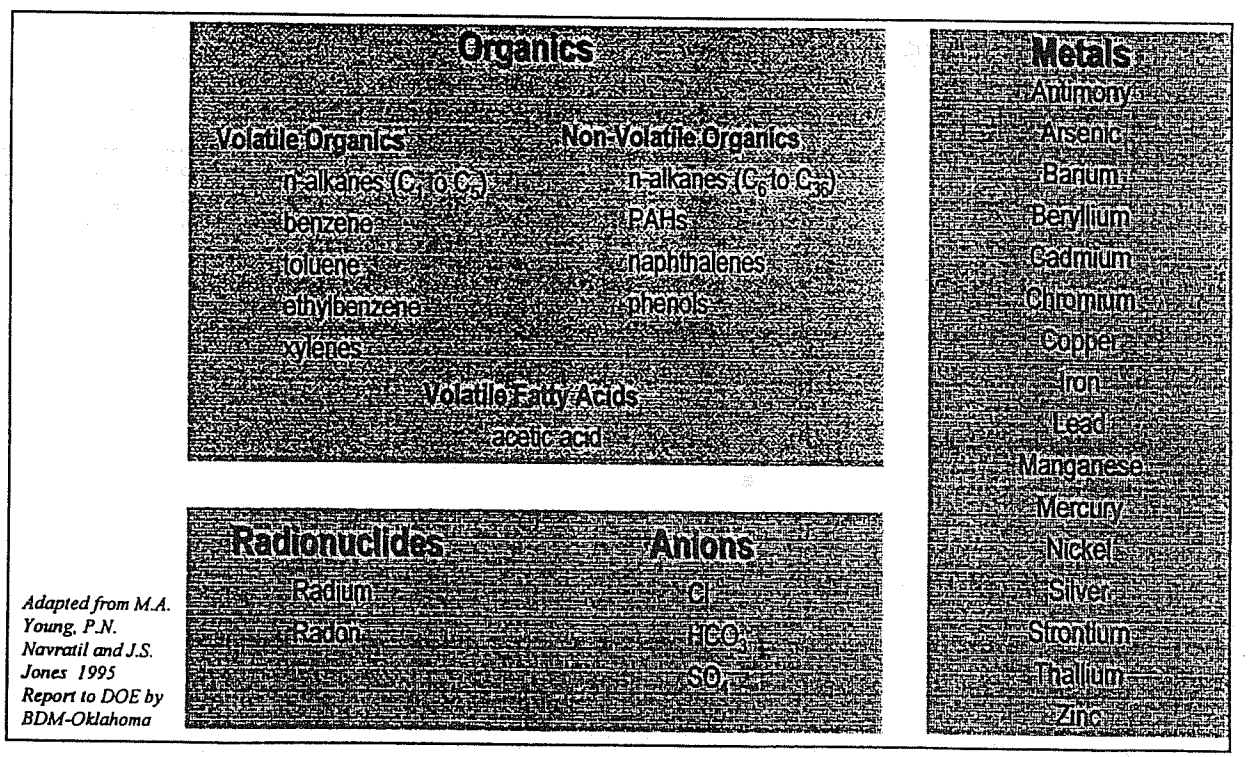


Figure 6: HUMASORB-S™ is Effective for Toxic Metals Removal from Spiked Water

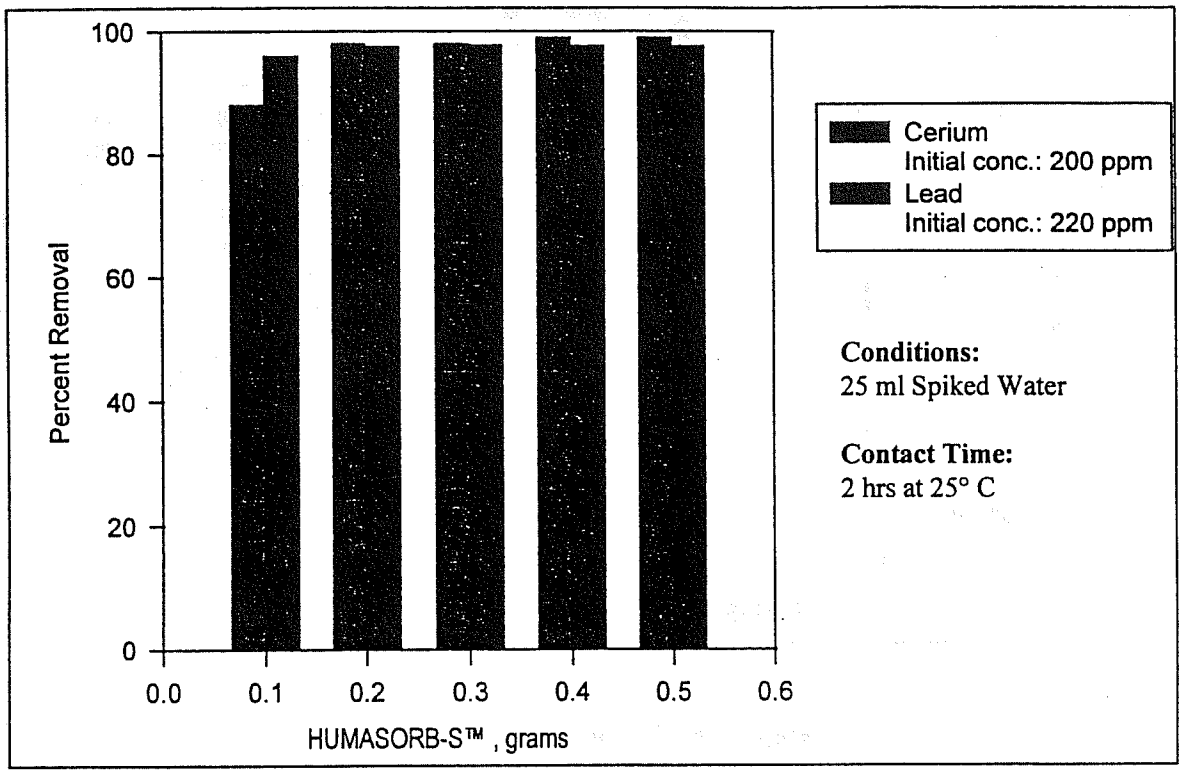
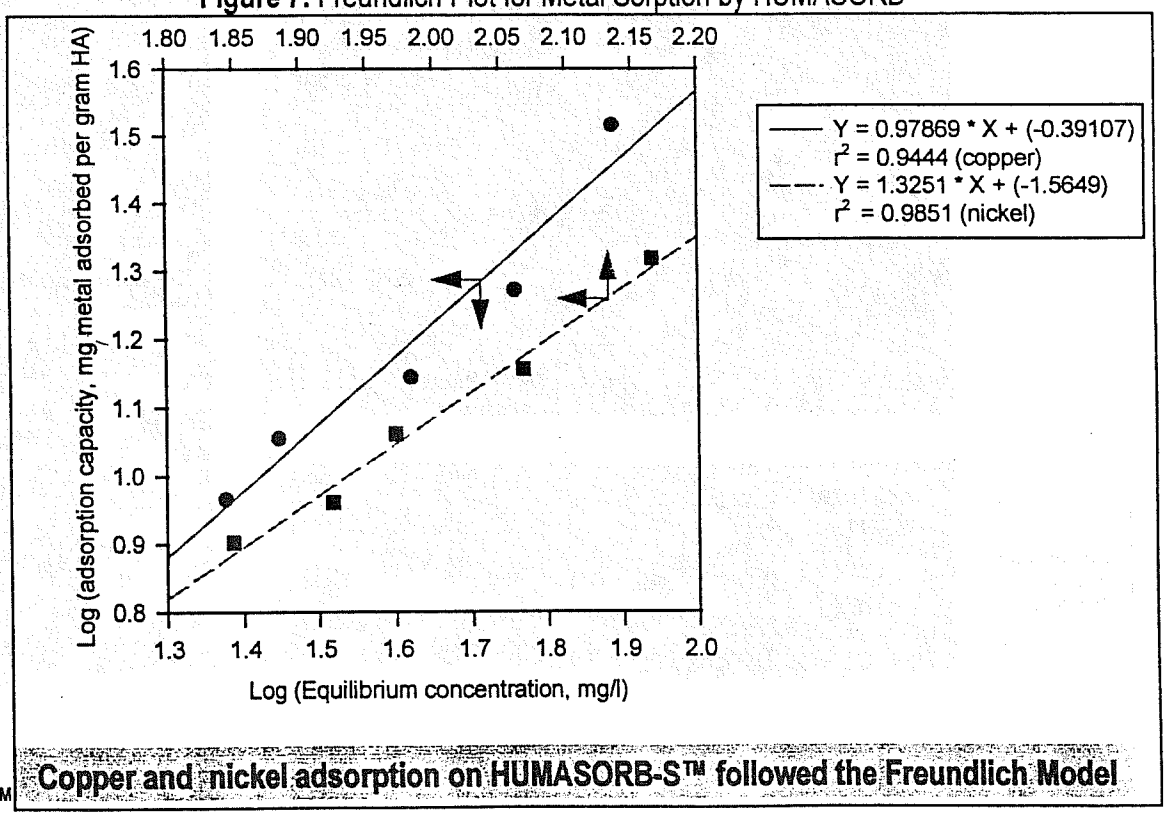


Figure 7: Freundlich Plot for Metal Sorption by HUMASORB-



S™ **Copper and nickel adsorption on HUMASORB-S™ followed the Freundlich Model**

Table 4: HUMASORB-CS™ Can be Successfully Used for Oil and Gas E&P Operations

TYPICAL METALS	RAW WATER	TREATED WATER
	ppm	
Aluminum	255	7.87 - B
Arsenic	.513	0.150 - U
Cadmium	1.99	0.0715 - B
Copper	198	0.287 - B
Iron	982	0.602 - B
Magnesium	417	271
Manganese	195	52.4
Potassium	9.21-B	3990
Zinc	555	48.1

B: Below method detection limit

U: Undetected

Figure 8: Organic Contaminant Removal Using Humic Acid

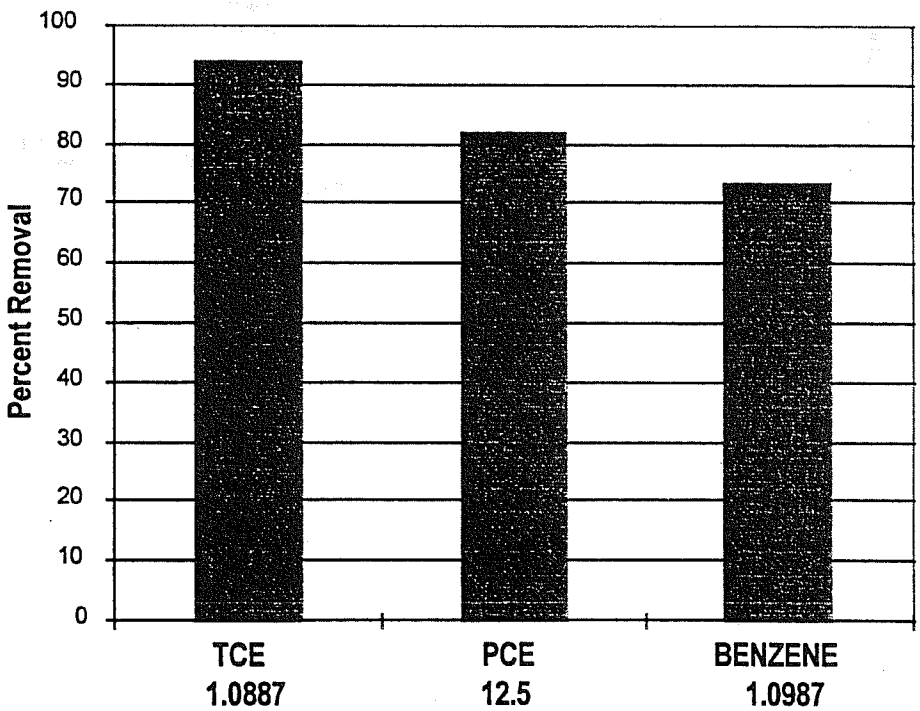


Figure 9: Scatchard Plot for Metal Sorption on HUMASORB-S™

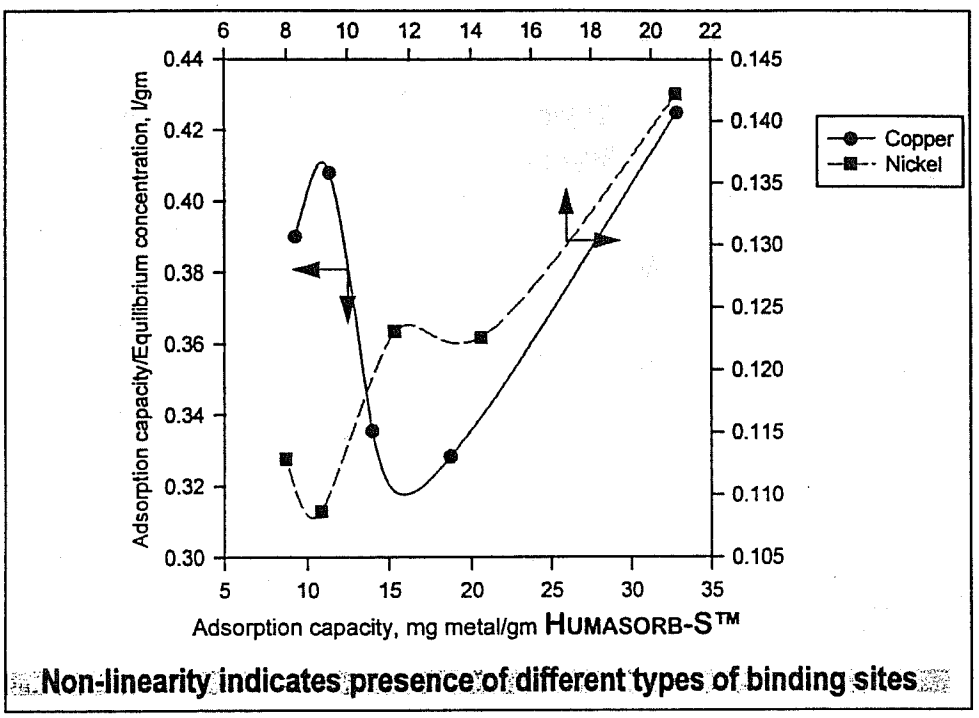


Figure 10: HUMASORB-CS™ is Effective for Chromium (III) Removal

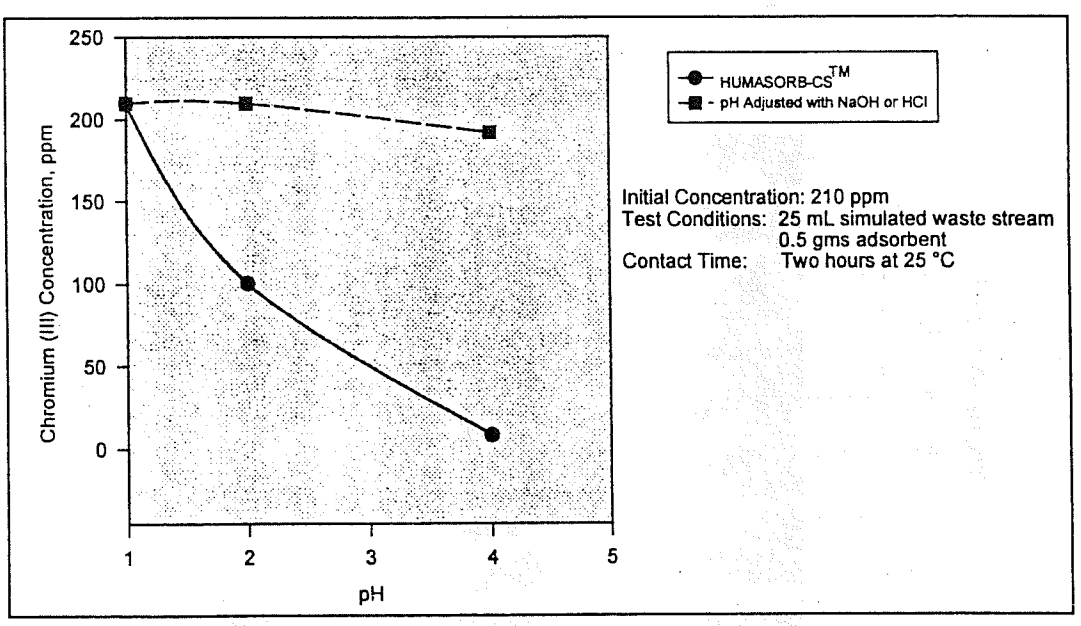


Table 5: HUMASORB™ Remediates Contaminated Groundwater Containing Metals, Oxo-anions, Radionuclides, and Organics

CONTAMINANT	SIMULATED WASTE Concentration, ppm			WASTE STREAM FROM A SUPERFUND SITE Concentration, ppm		
METAL CONTAMINANTS						
	Initial	Final	Removal %	Input	Output	Removal %
Aluminum	-	-	-	248	8.05	96.75
Barium	625	1.7	99.73	0.0878	0.116	-
Cadmium	115	7.9	93.13	1.95	0.0348	98.22
Calcium	-	-	-	444	252	
Chromium (III)	228	23	89.91	0.091	N.D.	-
Copper	134	1.9	98.58	178	1.62	99.09
Iron	500	56	88.8	922	60.4	93.45
Lead	220	5.3	97.59	0.205	N.D.	-
Magnesium	-	-	-	396	216	45.45
Manganese	-	-	-	190	46.6	75.58
Nickel	138	20.6	85.07	1.14	0.159	86.05
Selenium	-	-	-	N.D.	N.D.	-
Sodium	-	-	-	133	172	-
Zinc	-	-		530	45.1	91.49
OXO-ANIONS						
Chromium (VI)	60	< 1	> 98	-	-	-
RADIONUCLIDE CONTAMINANTS						
Cerium[2]	195	1.7	99.13	-	-	-
Strontium	200	3	98.5	-	-	-
Uranium	2000	N.D.	> 99	-	-	-
ORGANIC CONTAMINANTS						
Trichloroethylene	636	21	96.5	-	-	-
Perchloroethylene	114	8.5	92.5	-	-	-
Benzene	533	< 20	> 96	-	-	-

1. Chromium (VI) reduced to less toxic chromium (III)

2. Surrogate for plutonium

N.D. - Not detected

Table 6: HUMASORB-CS™ Enhances Distribution Coefficients

CONTAMINANT	EQUILIBRIUM CONCENTRATION IN THE LIQUID PHASE, ppm	DISTRIBUTION COEFFICIENT*, Kd ml/gm	pH
WITH HUMASORB-S ™			
Uranium	0.01	> 100,000	5.1
Lead	5	3500	2.25
Cerium	1.7	5600	2.5
Strontium	65.3	99	2.2
Chromium	138	54	3.2
WITH HUMASORB-CS ™			
Strontium	2.87	430	5.1
Chromium	22.65	566	3.2

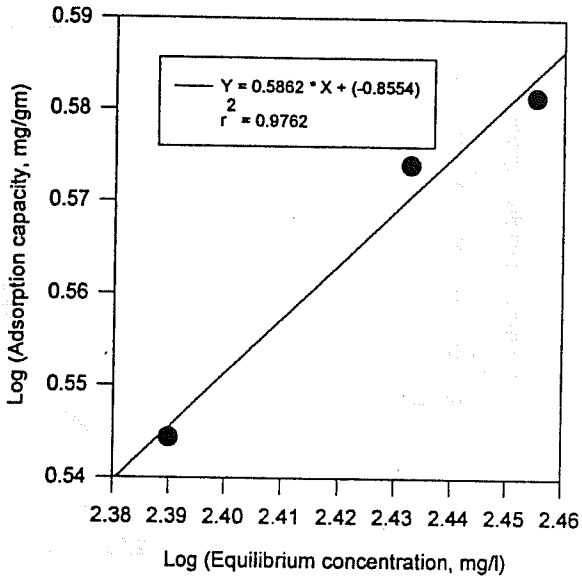
*: As determined from batch isotherm studies with only one contaminant present in the system

Table 7:HUMASORB™ Is Effective for Metal and Organics Removal from Different Matrices[1]

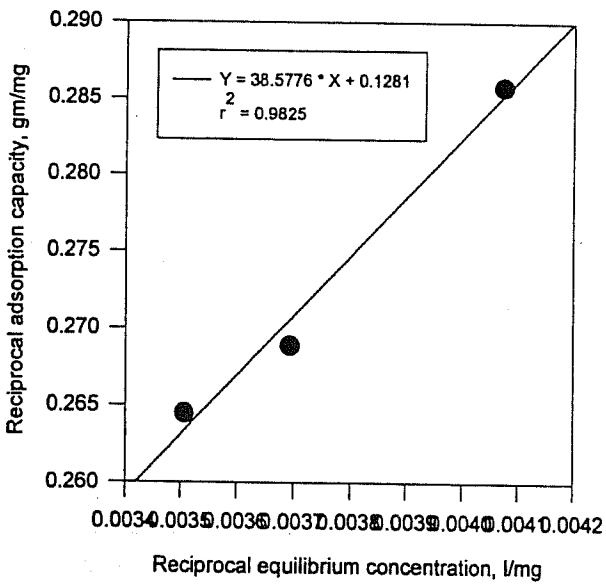
CONTAMINANT	SIMULATED WASTE[2] Concentration, ppm			WASTE STREAM FROM A SUPERFUND SITE[3] Concentration, ppm		
MIXED WASTE STREAM CONTAINING MULTIPLE METALS AND CHLORINATED ORGANICS						
	Initial	Final	Removal %	Input	Output	Removal %
Chromium (III)	88	< 0.5	> 99	-	-	-
Copper	98	< 0.5	> 99	-	-	-
Lead	18	< 0.5	> 97	-	-	-
Trichloroethylene (TCE)	140	1	99.29	-	-	-
Perchloroethylene (PCE)	26	N.D.	-	-	-	-

1: Source of Data: ARCTECH, Inc., 14100 Park Meadow Drive Chantilly, Virginia.
2: Simulated waste stream with three metal and two chlorinated organic contaminants present.
3: Treatability study using actual waste stream with multiple metals present
N.D. Not Detected.

Figure 11: Isotherm for PCE Adsorption on Humic Acid

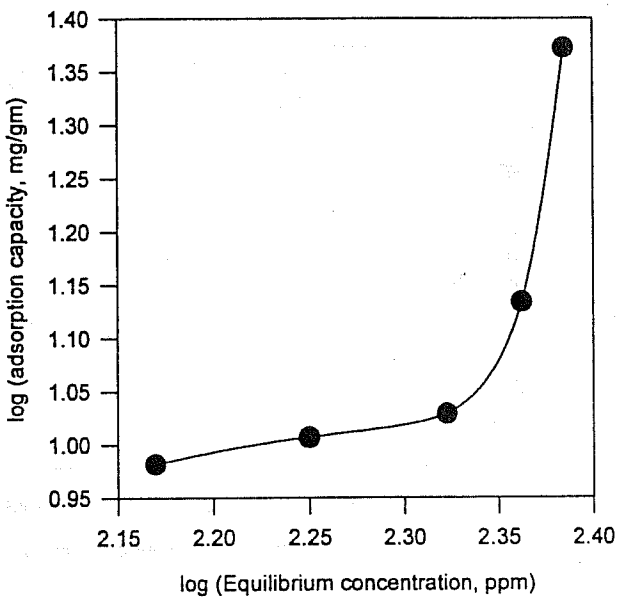


(A) Freundlich

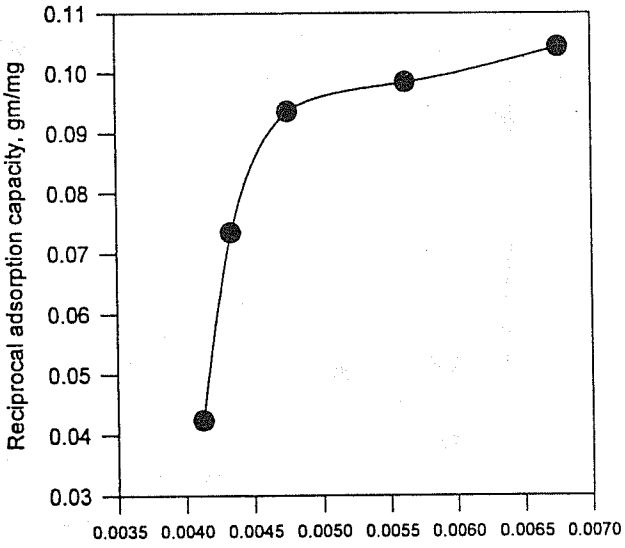


(B) Langmuir

Figure 12: Isotherm for TCE Adsorption on Humic Acid



(A) Freundlich



(B) Langmuir

Table 8: Freundlich and Langmuir Model Parameters

Contaminant	Freundlich	Langmuir
Copper	K = 0.4064 mg/gm n = 1.0218	K = 142.91 mg/gm b = 0.0029 l/mg
Nickel	K = 0.0300 mg/gm n = 0.7500	Negative values
PCE	K = 0.07691 mg/gm n = 0.6697	Negative values

Produced Water Treatment and Surface Discharge:

A Brief Comparison of Disposal Alternatives

Brad F. Simmons
RMI Environmental Services Inc.

The disposal of produced water has rapidly become a significant economic and environmental consideration for both onshore and offshore well operators, and now represents the largest source of waste in the energy industry. The Gas Research Institute (GRI) estimates that in 1990 the total volume of produced water from oil and gas operations in the U.S. was 14 billion barrels (1). Historically, the majority of produced water has been reinjected for disposal and enhanced recovery, or discharged into the ocean from production facilities with no treatment. However, increasing attention to the potential environmental impacts coupled with escalating capital and operating costs have propelled the research and development of other disposal options. The result has been the implementation of several treatment and disposal alternatives which are often utilized in combination with one another. The technical and economic comparison of several alternatives currently being evaluated is the topic of this paper.

Disposal Options for Produced Water

A brief description of each of the following produced water disposal alternatives, their associated treatment technologies, and the limitations of their application will be presented summarizing the assumptions and parameters used in the final evaluations. Advantages and disadvantages of each alternative address the areas of technical feasibility, regional and regulatory conditions, permitting and general economic guidelines.

- Subsurface injection
- Surface evaporation/enhanced solar evaporation
- Thermal evaporation
- Land application/constructed wetland treatment
- Freeze-thaw crystallization/surface discharge
- Hauling and off-site disposal
- Reverse osmosis treatment/surface discharge

Many disposal options are available to producers, however, this does not guarantee that any one of them will be a feasible solution from both an economic and technical viewpoint. The viability of each of the options is highly dependent upon the specific situation. Due to the topographical location and physical distances between wells, the collection of the water and the projected volumes to be delivered to a central point may be the most important considerations. Other factors that must be considered when evaluating any option, or combination of options, includes injection well drilling costs and associated risks, land availability, accessibility, proximity to commercial/independent disposal facilities, gas/water pipeline gathering systems, and the regulatory agencies with specific jurisdiction in the area. The key characteristics of each producing area can vary significantly by comparison with others nearby due to state, county, regional, and significant topographic boundaries and divisions.

Subsurface Injection

Historically, oil and gas producers have attempted to rely solely on well-established water disposal methods. Subsurface injection typically represents the simplest, most cost-effective disposal method and therefore, remains the mostly widely used by onshore producers. Once an injection well is permitted, drilled, successfully completed and operational, it can often require the least attention and maintenance, and consequently, may have a lower operating cost than the other alternatives. However, when factoring in the risk and initial capital cost to acquire a successful injector, it may represent more unknown economic and environmental risk than any of the other options.

Due to the recent increase in environmental awareness and its potential impact on subsurface hydrologic conditions, the use of reinjection has been limited or even prohibited in some areas. The increased demand for shallow water aquifers has focused regulators' attention on protecting water resources and water quality. The Safe Drinking Water Act requires that produced water be injected into Class II injection wells which usually restricts the injection into formations that contain water with a higher concentration of dissolved solids than that of the water being injected. This has forced producers to drill deeper, more costly injectors. Additionally, information on the deeper formations' permeability and porosity may be limited due to fewer penetrations and more scattered well control. The regulators also require that the injection pressures be monitored, and limit the bottom-hole pressures to prevent fracturing of the formation and contamination of other nearby zones. All these factors combined with the higher drilling cost represent a much greater risk of completing a successful injector, and may significantly limit its projected operational life.

Surface Evaporation/Enhanced Solar Evaporation

Another common disposal alternative is the use of surface evaporation ponds. Generally, evaporation ponds can be utilized to dispose of produced water, but, in cases with high water volumes and stringent regulatory requirements, evaporation may be limited, or dismissed as a viable alternative. Factors such as the impacts to local wildlife, groundwater resources, and regional aesthetics must be considered. Some areas require the surface impoundments to be double-lined with elaborate leak-detection systems, fencing, and bird netting which can more than triple the construction costs. Whereas in a nearby producing area, liners, fencing, and/or netting may not be required at all, or conversely, regulations may prohibit the use of ponds entirely.

Another limiting factor affecting the use of surface evaporation is its total dependence upon the regional evaporation rates of the specific area. Even oil and gas basins in arid regions of the south-central and southwestern U.S. may not have adequate evaporation rates to feasibly dispose of produced water. However, the natural evaporation rate may be enhanced cost effectively by implementing a sprinkler aeration system, and/or a solar salt gradient heat recovery system on the evaporation ponds. A relative cost comparison between natural and enhanced evaporation in a representative arid region of northwestern New Mexico will be addressed in the economic scenarios to be presented later.

Other disadvantages include the requirement for large, flat land areas, inconsistent year-round disposal rates, and the ultimate removal and disposal, or burial, of the dry byproducts. The consideration and resolution of these variables typically prohibits the use of evaporation ponds for the disposal of high volumes of produced water. However, when used in conjunction with other treatment disposal options, evaporation can be cost effective for the disposal of a small percentage of the total produced water volume as will also be discussed later.

Thermal Evaporation

Another means of evaporating produced water is by the use of a mechanical thermal evaporation system. There are an increasing number of mechanical evaporation technologies available for water distillation today, however, this evaluation will consider two basic designs which were the only ones identified as being utilized for produced water disposal. The first technology discussed is commonly referred to as "submerged-combustion" evaporation. Typically, natural gas is burned in a chamber which is submerged in the evaporator's water vessel and the resultant combustion gases are forced under pressure into the produced water. Steam pockets then form which migrate to the water surface and escape into the atmosphere. This unique design eliminates the

inherent scaling problems and loss of efficiency experienced with traditional evaporator designs which rely on a metal exchange surface to transfer the heat to the water. This design is also much more fuel efficient with consumptive rates of approximately 450,000 BTUs/barrel, as opposed to traditional designs which may require up to 650,000 BTUs/barrel, assuming both are single-effect units. However, the submerged-combustion evaporator's fuel cost typically prohibits its use as a disposal option except in very low water volume cases, or as with surface evaporation, in conjunction with other treatment disposal options. Also, depending on the size of unit, an air emission permit may be required for its operation which could limit, or prohibit, its use in specific areas. Lastly, the operator is also still faced with determining a means of disposal for the resultant concentrated brine (approx. 10% by volume of the feed).

The other thermal evaporative design to be addressed will be referred to as the "low temperature evaporative process", or more aptly the "Harris process" as per the developer of the technology, Harris Engineering of Cameron Park, California. In the Harris process, an airflow is induced through an evaporation chamber where a saturated downflow of slightly heated water droplets encounter the cross flow of air. The droplets are reduced in size and cooled via evaporation becoming slightly concentrated. The slightly smaller droplet is then captured, reheated and sprayed into the airstream again. This process continues until solidification as a salt slurry occurs(2). Because vaporization occurs in direct and sole contact with the airstream, as with the submerged-combustion design, evaporative surface fouling does not occur. In addition, the Harris process operates at low temperature levels enabling the utilization of low grade waste heat, thereby eliminating the high energy cost of the other evaporator designs. Waste heat sources may include pump exhaust, coolant heat, compressor heat, casing head gas and gasoline engine exhaust, and can be combined if necessary through a central manifold system. Another advantage to the process is that air emissions can be controlled, or even reduced at currently operating facilities, by a proprietary mist eliminator which captures particulate matter entrained in the airstream via wetted surfaces. With the addition of a final heat exchanger the process can be modified for the recovery of fresh water from the warm, humid effluent airstream. Lastly, this low temperature evaporative process and its efficient operating costs are very complimentary to other wastewater disposal technologies as outlined in the final economic comparisons.

Land Application/Constructed Wetland Treatment

At sites where the produced water quality meets the particular regulating agencies' water quality requirements it may be applied directly to the land, or used to create a wetland as authorized under a surface-discharge permit. Although there has been a relatively limited amount of research performed on the use of

wetlands to remove dissolved contaminants from produced water, numerous wetland designs have proven their capabilities for the treatment of biochemical oxygen demand, suspended solids, nitrogen, phosphorous, pathogens, and trace metals. The limited application of "constructed wetlands" technology for the treatment of produced water have achieved efficient reductions of specific radioactive ions, hydrocarbons, heavy metals and sulfides to meet effluent discharge limits (3).

These projects rely primarily on the cascading aeration of the waters through multi-level cells which are cultivated with natural wetland habitat. The removal of the dissolved ions is accomplished through a combination of mechanisms depending upon the produced water's total dissolved solids (TDS) concentration, temperature, pH and ORP, discharge flow rates, flow turbulence, and the treatment cells' permeability and soil chemistry. All of the following physical mechanisms have varied effects on the recovery and efficiency of a wetland treatment system (4): filtration and sedimentation of solids, chemical precipitation of low solubility salts and metals by oxidation, coprecipitation with salt or metals (such as radium 226), absorption of hydrocarbons and metals, uptake by vegetation, microbial interactions, and volatization (such as volatile hydrocarbons and sulfide). Precipitation and coprecipitation are primarily controlled by carbonate equilibria and the reactions that result from offgassing, precipitation and dissolution reactions, and the wetland biological processes. These reactions are responsible for the removal of low solubility salts, (ie. barium sulfate and calcium phosphate), elemental sulfur, as well as the co-precipitation of radium sulfate.

Although these wetland systems can be adapted for high throughput volumes, and appear to be very cost competitive from an initial capital and operating cost basis, there are a number of problems with maintaining consistent results. Uncontrollable variables in the system's open design result in complicated kinetics which change significantly with the seasons, or even possibly over the course of a day. These fluctuating parameters directly relate to the expected removal efficiencies and dependability of the system, and necessitate maintenance where possible. The development of channels, dead zones, and significant accumulations of removed contaminants must also be prevented to maintain the desired effluent results.

Due to this technology's limited treatment abilities, its application will remain limited to areas with less stringent guidelines than most, or as a pretreatment process in conjunction with another disposal technology. It also has the inherent environmental problem of dealing with the contaminated soils and biomass accumulated in the wetland. The combination of these problems will greatly limit, or possibly prevent, the use of constructed wetlands as a produced water treatment option in the foreseeable future.

Freeze-thaw Crystallization and Surface Discharge

By freezing brackish water during the winter and draining the resultant brine from the ice pile, an accumulation of purified ice can be collected. In the spring as the temperatures increase and the ice melts, the dissolved solids that were originally present in the brackish feed will be significantly reduced. Typically, over 95% of the dissolved solids are removed enabling the surface discharge of the resultant purified water under an NPDES permit issued by the state or EPA.

This process has been known to exist throughout most of history, but only over the past twenty years has any significant research taken place to utilize this natural phenomenon as a disposal option for produced water. As early as 1939, Heller of the U.S.S.R. was able to treat brackish groundwater for agricultural use in desert areas from 15,000 to 400 ppm TDS (5). He concluded that as ice forms from brackish water and is subjected to freeze-thaw cycles, the salt concentration is significantly reduced. More recently in Wyoming, significant research for the separation of dissolved solids from water by natural freezing has been studied and proven effective. Some of the most successful research was conducted through the University of Wyoming by Dr. Don Stinson of Laramie. In 1973, a pilot test was conducted on the Big Sandy River to evaluate the application of freeze-thaw to a stream flowing 30,000 acre ft./yr. of 8000 ppm TDS into the Colorado River system(6). The pilot was designed to handle 2,500 gpm in an area of approximately 20 acres. Effluent water qualities from the thawing of the ice mass were typically well below the most stringent Drinking Water Standard of 500 ppm TDS, and at one point got as low as 27 ppm. This represents a 99% reduction in the dissolved solids and was comparable with samples taken from snow drifts of the same age.

In addition to demonstrating dramatic reduction efficiencies of total dissolved solids, Stinson's research also confirmed that the process is effective in removing salts, acids, bases, sugars, and organics from water. In areas where land is readily available and a sufficient freezing period exist this process offers the lowest cost technique for desalting water. The impoundment construction and equipment cost are basically equivalent with those of a surface evaporation pond with an enhanced aeration system. This creates an ideal situation for the use of solar evaporation in the warmer summer and fall months, and freeze-thaw during the winter and spring. The net result is a consistent year-round disposal process which can increase the disposal capacity of a surface pond by several factors. The disadvantages of freeze-thaw are also the same as those of surface evaporation as discussed earlier, however, when used in conjunction with other treatment disposal options, a freeze-thaw/enhanced evaporation system can be very cost effective. In consideration of this option's total dependence on regional climatic conditions, the projected costs of a northern Rockies versus a southern Rockies site are presented

in the economic analyses, demonstrating the substantial cost differences possible from one area to another.

Hauling and Off-site Disposal

Hauling and off-site disposal is utilized in some capacity by most operators in conjunction with one of the other methods. Water truck hauling is used as a means to transport the produced water to a company-owned, or commercially operated injector or evaporation disposal facility and is usually limited to producing sites with lower water volumes, and easily accessible locations.

The major disadvantage of this option is the cost. Transporting water by hauling can triple the overall disposal cost, and the operator still must incur an additional cost for commercial disposal, or the other costs associated with capitalizing and operating a company-owned disposal facility. Therefore, in areas where it is permitted and topographically feasible, operators typically construct a pipeline gathering system to collect the produced water to a central point. Hauling to another site does not eliminate the operator's liabilities of handling the water on public roads, or as they relate to the final disposal site. The prevention of fugitive dust from truck traffic, and road repair and maintenance can also be very costly. In the Four Corners region of the San Juan Basin, hauling costs can range from $2.00-$4.00/bbl., depending on the time of the year and distance to the ultimate disposal site(7). Even when considering these issues, truck hauling may be the only alternative for gathering and transporting the water from the producing wells.

Reverse Osmosis Treatment and Surface Discharge

Since a major component of produced water is relatively high dissolved solid concentrations, most treatment systems used for surface discharge will have to incorporate a desalination technology to reduce the concentrations to dischargeable levels. These include distillation, electrodialysis, and reverse osmosis (RO). At this time, the only one of these technologies which has been implemented and demonstrated on a full-scale basis is reverse osmosis. Due to the environmental concerns and economic limitations commonly associated with the other water disposal options, RO treatment and surface discharge of the majority of the produced water from a site is highly attractive. Transporting the water can be reduced or eliminated, and the environmental impact is greatly reduced. The process can also result in the recovery of purified water for reuse in another surface application, such as farming/ranching, aquaculture, or an alternate recreational use.

The following outlines treatment methods which have been established as the required components of a proprietary RO treatment process for the disposal of produced water. The data and research discussed is based upon the utilization of

this integrated system at several sites by RMI Environmental Services, of Farmington, NM, specifically for the treatment and disposal of produced water.

The technologies of the RMI process can be divided into two categories and grouped together as follows; A) Pretreatment; utilizing flotation/aeration, solids clarification and filtration, ion exchange/softening, and chemical addition and treatment, and B) total dissolved solids reduction utilizing reverse osmosis (8). Feed water pretreatment is probably the most important factor to insure a successful RO plant. If pretreatment is inadequate, the RO will become fouled, because in addition to TDS removal the RO membranes will also reject all suspended solids, colloids, and metals. Pretreatment can also control and decrease the tendency of scale formation on the membrane resulting from the increased salt concentrations as fresh water is removed.

The first step of pretreatment is the removal of any free hydrocarbon or other insoluble organics. Dissolved air flotation, or induced air flotation, is typically used to separate the oil and organics from the water. This treatment also results in the oxidation of any ferrous iron to ferric hydroxide which can be removed by filtration further downstream. In produced waters with particularly high concentrations of suspended solids, clarification may be required by utilizing an inclined-plate clarifier. The next pretreatment step can be accomplished by using a number of different filtration technologies in series and should be evaluated each time based upon the quality of the specific produced water being treated. Multi-media or sand filtration may be the first filtration stage. Then the media filter effluent passes through polishing cartridge filters. Often the effluent from the polishing filters may be fed directly into the RO unit, however in most applications, more consistent results and better overall recoveries will be possible if an ultrafiltration system is used ahead of the RO. Next, the produced water may need to be softened, or have some specific ions removed to prevent scaling in the RO. This can be accomplished by utilizing a softener media bed, or specific ion exchange resin as dictated by the inlet water quality. Finally, chemical pretreatment is usually necessary to control the scaling tendencies of compounds as they are concentrated in the RO. Sulfate scales can often be controlled with chemical antiscalants, and calcium carbonate scale with the injection of acid to lower the pH. It may also be necessary to continuously inject a biocide, or shock treat the system periodically to prevent fouling of the RO by bacterial growth.

The key treatment technology of the process is the use of reverse osmosis for the removal of dissolved solids in order for the permeate (purified effluent) to be discharged to the surface. When utilizing RO for the treatment of produced waters, careful consideration must be given to the design of the unit and modeled such that realistic recovery rates and minimum effluent water qualities can be met. The RO system should also be designed with as much emphasis placed on an effective cleaning system as the configuration of the RO itself. If an ultrafiltration

system is used as pretreatment, it also must be equipped, or may share, a cleaning system with the RO.

The biggest disadvantage to utilizing reverse osmosis for the treatment of produced water is its inability to dispose of 100% of the total volume. The overall recovery of any RO treatment system will be dependent upon the water quality, temperature, permit effluent requirements, and site specific economic limitations. On the projects where RMI has utilized this integrated RO process, discharged recoveries consistently range between 70-75% of the initial feed stream volumes, therefore, RO treatment must be combined with another disposal option to handle the remaining "concentrate" stream. Surface evaporation, deep-well injection, or thermal evaporation are the most common options combined with RO and are each addressed separately in the economic scenarios presented later. Other issues which can complicate the decision for utilizing RO include the experienced labor requirements, projected production volumes and life of the field, well groupings and associated gathering systems, access/topography, and the permitting requirements. Permitting for the surface discharge of the treated water is typically authorized under the EPA administered NPDES program.

RO treatment may represent the most flexible and economic alternative for the disposal of produced water. Initial capital costs are often much lower than those of drilling and equipping an injection well, and drilling risks are eliminated. Other disposal methods such as surface evaporation, freeze-thaw crystallization, and/or thermal evaporation can have signicificantly higher capital costs than a RO depending on regulated requirements. Although operating costs tend to be much lower for these options which require less maintenance and attention, the RO operational costs can be reduced by utilizing an automated control system (SCADA) to control some of the system functions with a remote computer. An effective SCADA system may add as much as 10% to the initial capital cost, but will result in a savings of 20-25% on the monthly operating cost (9). The RO system can be relocated and with limited modifications may treat water at another site. Finally, at a time when recycling our natural resources is so highly attractive and logical, and clean water represents such a precious commodity in arid regions around the world, the RO treatment process can transform produced waste water into a valuable asset for reuse and to replenish runoff.

Economic Analyses

As you would expect, making broad analyses concerning the economic feasibility of the various produced water disposal options can be very vague and inconclusive. A detailed evaluation must be performed on a site-by-site basis and should consider all of the related factors. Although the economic comparisons rely upon specific assumptions, the relative disposal cost can be predicted. More precise projections could be extrapolated by making the necessary adjustments to cost figures which were the basis for these comparisons.

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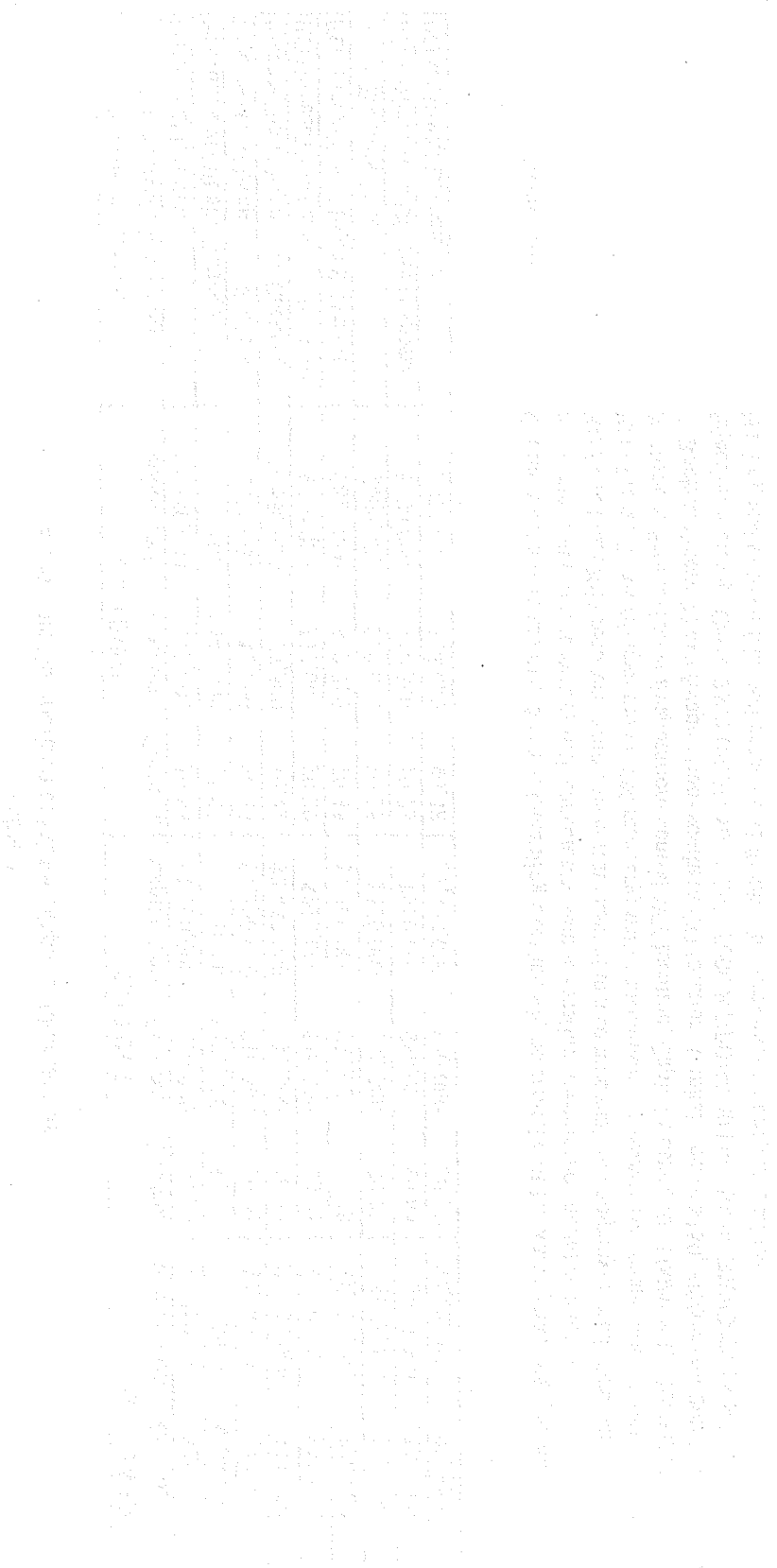
Table 1
Economic Comparison of Water Disposal Alternatives

Treatment Capacity Alternative/Combination	2,500 BWPD			5,000 BWPD			10,000 BWPD		
	Capital Cost	Op.Cost	Cost/bbl.	Capital Cost	Op.Cost	Cost/bbl.	Capital Cost	Op.Cost	Cost/bbl.
Deep Well Injection	$1,350,000	$18,000	$0.53	$1,500,000	$20,000	$0.30	$1,750,000	$25,000	$0.18
Hauling and Off-site Disposal	$0.00	$141,000	$1.85	$0.00	$282,000	$1.85	$0.00	$564,000	$1.85
Freeze-Thaw/ Evap N. Rockies	$600,000	$8,500	$0.24	$1,300,000	$10,500	$0.21	$2,180,000	$12,500	$0.16
Freeze-Thaw/ Evap S. Rockies	$1,450,000	$7,500	$0.42	$2,450,000	$9,500	$0.33	$4,750,000	$11,500	$0.30
RO+FreezeThaw/ Evap N. Rockies	$550,000	$13,000	$0.29	$925,000	$16,500	$0.21	$1,400,000	$20,000	$0.14
RO+FreezeThaw/ Evap S. Rockies	$825,000	$12,750	$0.35	$1,300,000	$21,000	$0.28	$1,975,000	$26,000	$0.19
RO w/Existing Injector	$400,000	$20,000	$0.35	$550,000	$32,000	$0.27	$675,000	$45,000	$0.18
RO w/Hauling to Off-site Disposal	$400,000	$48,500	$0.73	$550,000	$90,000	$0.65	$675,000	$163,500	$0.57
RO w/HERM Evaporator	$875,000	$14,000	$0.38	$1,425,000	$20,000	$0.29	$2,425,000	$25,000	$0.22

Assumptions:

Capital Cost amortized over 5 years; Operating Cost/month; no capital cost for water gathering system.
RO / Injection (70% recovery) with concentrate sent to existing injector (no capital cost for well).
RO / Hauling (70% recovery) with concentrate hauled to a commercial, or company-owned, disposal site.
RO / Freeze-Thaw /Evaporation (70% recovery) with concentrate to freeze-thaw / evaporation system.
N. Rockies Freeze-Thaw/ Evaporation- central WY location; Capital Cost= $100,000/acre for 1000 BWPD capacity.
S. Rockies Freeze-Thaw/ Evaporation- southern CO location; Capital Costs= $150,000/acre for 200 BWPD capacity.
Injection Well Op. Costs: 2500 BWPD/$0.23 bbl.; 5000 BWPD/$0.20 bbl.; 10000 BWPD/$0.15 bbl.
Hauling and Off-site Disposal assumes $1.85/bbl. for transporation and disposal fee.



Induced Gas and Sparging Flotation

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Abstract

Introducing micro-fine bubbles has been one of the most widely used tools for oily water separation. How they are created and introduced into the oily water stream varies quite a bit. The key to good separation is to create the smallest gas bubbles possible and introduce them into the waste stream in an efficient manner for maximum mixing and retention time.

Another important tool used in oily water separation is coalescing media. When oil droplets flow through this media they will grow in size. The type of media used and the way it is designed into a separator varies a bit. When the media is used correctly good oil separation will occur.

The technical design of flotation equipment has relied on the principles of Stokes Law. Oil droplet size and density affect the rate at which the oil will rise to the surface of water. Increasing the size and decreasing the density of an oil droplet will make it rise faster. The use of gas flotation and coalescing media is based on Stokes Law. Micro-fine gas bubbles will attach to an oil droplet and decrease the density of the oil droplet. Coalescing media will help to grow oil droplet size.

INTRODUCTION

Oil producers rely on effective separation and treating systems, such as treaters (crude dehydration), separators, desalting units, and several other types of equipment in order to sell the oil and gas. Worldwide oil production of crude oil was about 22 billion BPD in 1995 (1). Because there was a lot of water being produced with this oil production, the treatment of the produced water to an environmentally acceptable level has become very important in today's world. The maximum amount of oil that is acceptable in produced water discharged overboard is being lowered around the world. It has been lowered to 29 ppm of oil offshore USA.

The standard treatment of produced water is normally through skimmers as well as flotation units as final polishers of the water. Flotation units are necessary for a few reasons. The amount of oil which is still within the water after separation by normal skimmers is not low enough to meet the standards. Oil particles tend to be sheared into a very small oil droplet size of 50 microns or less when passing through flow lines and production equipment. Reverse emulsion is also a problem, whereby a small globule of oil is suspended inside a globule of water. The two products normally will not separate in typical separators, therefore causing the oily water globules to be discharged with the water phase increasing the oil content level in the produced water.

It is essential that the producers of oil use economical and efficient ways to treat these produced waters. The search for new technology has been ongoing for years now and many changes have been made in the type of equipment used to treat the produced water. The latest change for MONOSEP has been the use of sparging technology. The following paper will review existing technology and explore this new technology to compare it to other water treating systems.

EXISTING FLOTATION UNITS

MONOSEP Corporation was formed in 1972 to build flotation units. Its first product was a unit called the "MONOSEP" which was a single cell separator. The system was simple in its design using a centrifugal pump to force water through an orifice which brings in vapor gas from the unit forming many fine bubbles. This eductor introduces the bubbles into the total water stream helping float the oil to the surface to be separated from the water. A coalescing media was also used. Over the years many of these units were used in the Gulf to treat discharge water. Some of the units are still in

operation and doing a good job of removing the oil from the produced water.

Many induced gas flotation (IGF) systems on the market have been derived from this original system. Units with multiple cells, paddles, weirs, diverters, coalescing media, and other designs have been developed over the years.

GAS SPARGING FOR FLOTATION

A new type of gas flotation separator has been developed by MONOSEP which uses only low pressure gas to produce the micro-fine bubbles necessary for gas flotation. Gas sparging is something MONOSEP has been working on since the early 1990s. The first system was installed in a waste water tank at a shipyard. Systems have been installed in older existing vessels to help with the removal of the small oil droplets. Over the last few years quite a few systems have been installed into existing vessels and tanks; also several new vessels have been built.

Gas sparging is simple and effective. MONOSEP has worked with a major oil producer to develop a system using gas sparging for flotation. It requires no electricity to power motor or pump systems. It requires 2 - 3 scf of gas per barrel of water per day. Therefore a 1,000 BPD unit would use no more than 3,000 scf per day. Gas sparging has been introduced into the system to do away with eductors and recycle pumps. The gas vapor can be recovered by a vapor recovery compressor on location.

Sparging rate and surface area of tubes

The size of the gas bubbles created by the sparging tube is dependent on the exit velocity of these bubbles. The right pore size of the tube and the correct gas flow will create a desired exit velocity for the smallest bubbles. A low gas flow with a fine pore size will lead to a smaller bubble size.

To size a sparging tube for a vessel the following information is needed: the gas flow rate, liquid pressure at the sparger, temperature of the water, specific gravity of the water and the desired exit velocity at the tube. These can be used to calculate the sparger surface area required in square feet. Once the required surface area is calculated a sparging tube can be sized.

A secrecy agreement between a major oil company and a few

equipment suppliers will not allow for the selected gas flow and exit velocity to be given.

The ACFM is calculated from the liquid pressure at the sparging tube. To determine the liquid pressure at the sparging tube (P) take the liquid head in feet x 0.433 x specific gravity of the produced water. If the vessel is pressurized add this pressure to the liquid head pressure. Take the desired SCFM of the gas flow to the tube and the temperature °F, (T). Calculate the ACFM using the standard formula, then use the desired exit velocity expressed in feet per minute (FPM) to determine the sparger area (A).

$$ACFM = \frac{SCFM x 14.7}{14.7 + P} x \frac{460 + T}{520}$$

$$A = \frac{ACFM}{FPM}$$

The size of the sparging tube is now selected from the pore size and tube surface area. Check the manufacturer's data to confirm the correct size tube necessary to give the calculated (A)(2).

New equipment with sparging technology

The latest vessels designed utilizing gas sparging are vertical systems. The CYCLOSEP and the SPINSEP are the two vessels MONOSEP has designed. Vertical vessels seem to be more efficient because the distance between the oil pad and the clean water outlet is maximized, and the liquid head pressure on the tube is also maximized. Also the more distance the water has to flow through a column of bubbles the more oil will be removed. Important in the design is also the use of a coalescing media. In a vertical vessel the coalescing pack section can be easily installed. With the sparging tubes underneath the pack, the bubbles help keep the pack clean.

The SPINSEP inlet piping has a spinner design inside the vessel. This inlet spinner has a sparging tube inside which mixes many micro-fine bubbles into the total stream. If enough inlet pressure is available, an eductor type spinning system can be installed within the vessel. With the

eductor system within the vessel, the distance from the orifice to the discharge point is very close. This creates a smaller size bubble for better attachment to oil droplets.

This inlet piping is installed about a foot below the liquid level. It is designed so that the water and gas/oil mixture spins around the inside of the vessel shell. The spinning motion helps the bubbles come in contact with more oil droplets due to the fact that these bubbles cover more area as they spin to the top. A pack section is installed to help grow the smaller oil droplets. There are several gas sparging tubes below the packing to help clean the packing and carry the oil to the surface to be skimmed over into the oil bucket. See Figure 1.

The CYCLOSEP features a Hydrocyclone in the inlet piping. This Hydrocyclone helps with solid and oil separation before it enters the flotation zone. A solids hopper will catch the solids to be drained out the bottom of the vessel. The CYCLOSEP features a coalescing media and several sparging tubes for flotation. The oil is skimmed off the top of the vessel into an oil bucket. See Figure 2.

Practical field experience

Setting the gas flow rate for the correct bubble size in the field takes experience. In an atmospheric vessel one can see the bubble pattern and set the gas flow based on the observation. In a pressurized vessel one must rely on a pressure gauge and an understanding of pressure vs bubble size. Too much pressure will create large bubbles, not enough pressure and no bubbles will be created.

Gas sparging is not the answer for every location. Water chemistry can have many different effects on the sparging tubes. The SST sparging tubes may plug from within with dirty gas or scale on the outside which prevents the tubes from developing the micro-fine gas bubbles that are required. The scaling of sparging tubes is the biggest problem in the field. Some waters produce scale more than others. This scaling tendency should be corrected if possible or sparging should not be used. Most of the systems have been designed to allow the installation of a recycle pump system to introduce the gas bubbles if the tubes become a plugging problem. The connections are installed in the vessel at the time of construction for future connection of a recycle pump and eductor system. With over 25 units installed or modified with gas sparging only three have had to be converted to eductor systems at this time.

There have been design changes to our standard eductor system to allow us to force gas directly into the recycle eductors. This design has helped with the removal of soluble oil from the produced water streams. The first system we designed was for a major tire company. Three 10,000 bbl/day pressurized VEIRSEP flotation units where built to remove Benzene from their waste water stream. The system worked great reducing the level of Benzene from 200 mg/l to less than 1 mg/l. Gas sparging should have the same benefits for Benzene and soluble problems. Soon, MONOSEP hopes to test the sparging system for Benzene stripping and soluble removal.

SUMMARY

MONOSEP is very confident that sparging systems are efficient and economical. Sparging is efficient in that the system creates micro-fine gas bubbles for good oil flotation and separation. There is a great cost savings in not having to run cable trays and wires and install motor starters for the motors to drive the pumps for a recycle system. On locations without electricity, the sparging system becomes essential to meet the strict discharge limits.

Sparging systems have proven to meet the discharge limits. Sparging systems cost less than recycle systems. Sparging systems will be the answer for many oil producers as they try to economically clean their produced water to meet the discharge limits. The future for sparging systems looks very good.

Table 1
Sparging Retro-Fits in Service as of mid 1996

SIZE AND TYPE	LOCATION
5M Multisep	EC 564
3M Monosep	EC 534
1M Monosep	EI 247
10M Monosep	EI 215
5M Veirsep	WD 97A
30M Skimmer	SP 37E
1M Pacsep	EI 45
3M Separator	Galv. 255
10M Separator	SP 69
3M Cyclosep	WD 83 E
3M Cyclosep	Brazos 397
15M Skimmer	SMI 80
3M Veirsep	EI 296
3M Mini-Veirsep	WC 98
10M Tridair	EI 330C
10M Chemlink	SP 37E
20M Skimmer	SP 86C
10M Multisep	EI 341A
Skimmer Tank	MP 6A

Table 2
New Sparging Systems in Service as of August 1996

SIZE AND TYPE	LOCATION
3M Cyclosep	VK 24
3M Cyclosep	EI 108
2M Cyclosep	Mobile 960
3M Spinsep	Galv. 393
5M Veirsep	Verm 252
3M Cyclosep	WC 504A
5M Veirsep	EC 14
40M Veirsep	Bay Marchand C&I
5M Cyclosep	WC 599A
5M Veirsep	Verm 252
5M Cyclosep	MP 223A
5M Spinsep	Verm 279
5M Cyclosep	WC 504A
1M Spinsep	GB 388

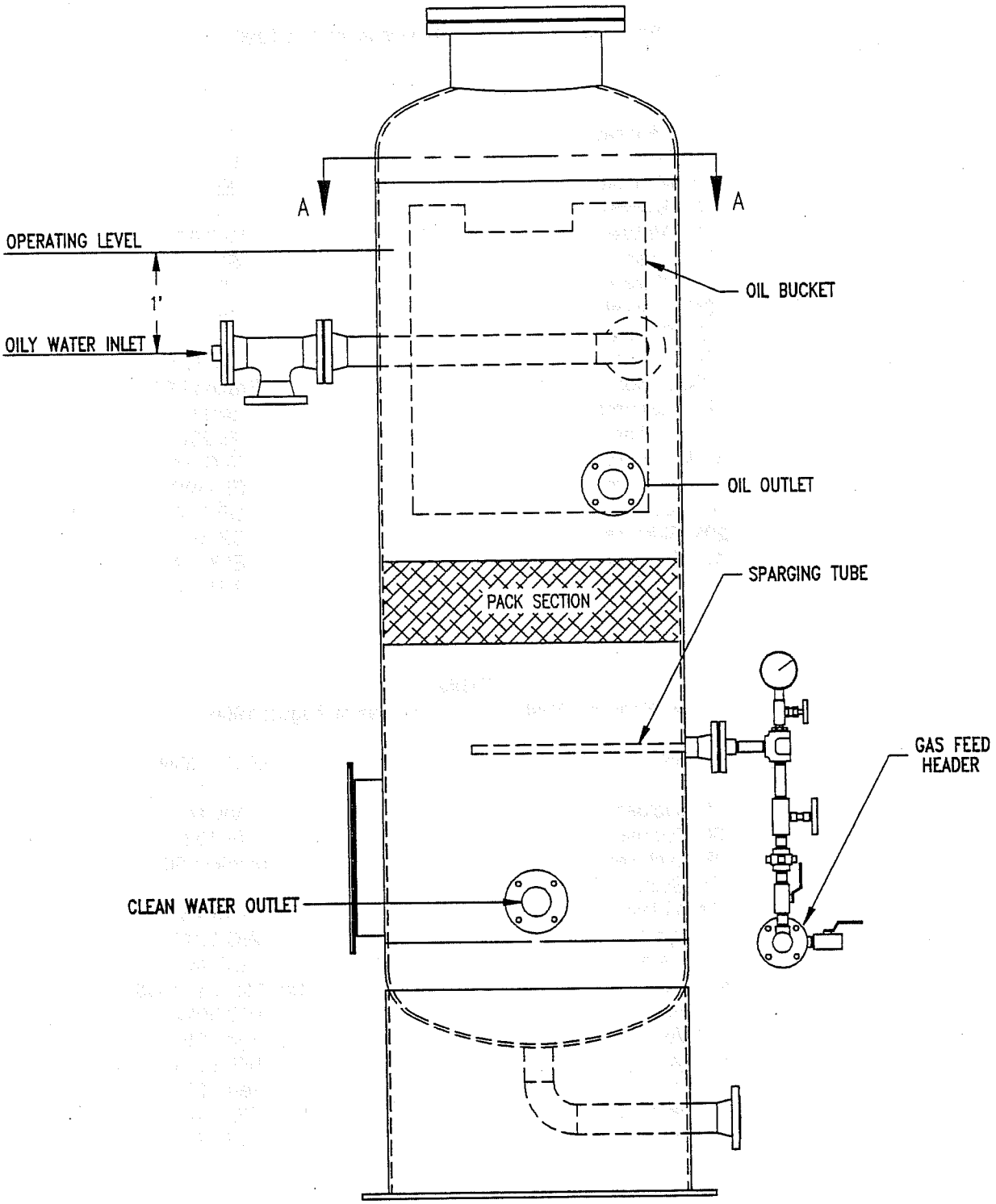

Figure 1. Spinsep

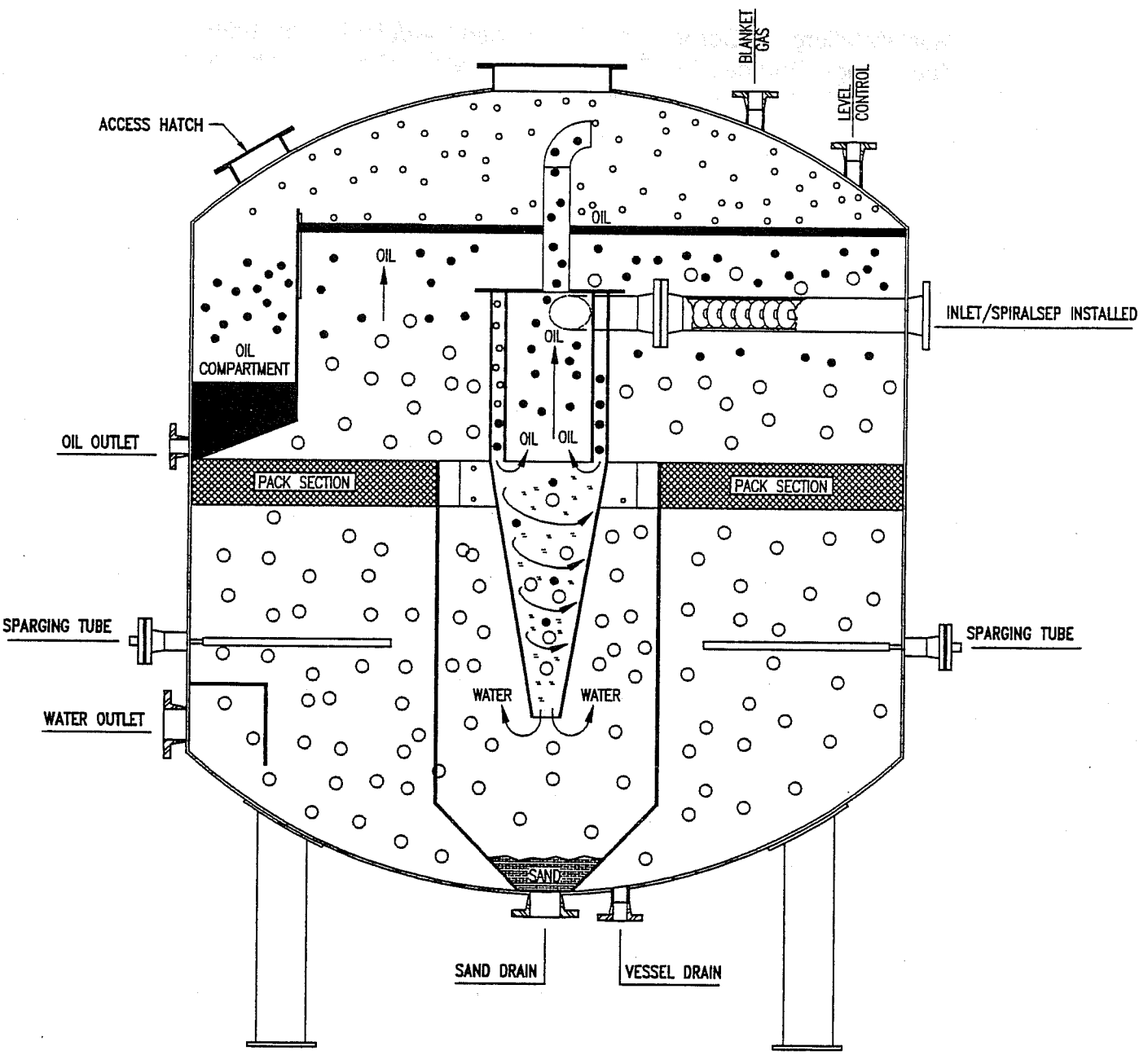

Figure 2. Cyclosep

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Field Demonstration of the Freeze-Thaw/Evaporation Process for the Treatment of Produced Waters in the San Juan Basin of New Mexico

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Abstract

Historically, treatment utilizing freeze-crystallization has been an economically proven method for purifying most waters. Water purification using naturally occurring freezing is an economic and attractive process in oil and gas producing regions where climatic conditions seasonally promote freezing. Research sponsored by Amoco Production Company, the US Department of Energy, and Gas Research Institute to develop a commercially-economic natural freeze-thaw/evaporation (FTE) purification process for produced waters has been conducted since 1992. Preliminary FTE field demonstration results from northwestern New Mexico during the winter of 1995-96 indicate significant and simultaneous removal of salts, metals, and organics from produced water. Despite the unusually warm winter, process yields demonstrate disposal volume reductions on the order of 80% and confirm the potential for economical production of water suitable for various beneficial uses. Total dissolved solids concentrations of the FTE demonstration streams were 11,600 mg/L (feed), 56,900 mg/L (brine), and 940 mg/L (ice melt).

INTRODUCTION

Oil and gas produced water management costs contribute to the overall cost of energy production. Water disposal costs are particularly significant in coal bed methane production. Since future domestic energy production will be increasingly dependent on production from unconventional sources of oil and gas, such as coal bed methane, and from economically marginal formations, water disposal/management costs are an issue of growing importance.

The use of freeze-crystallization is a low-cost, energy-efficient method for purifying water. Freeze-crystallization has been shown to be effective in removing a wide variety of constituents from water. Water purification by using natural conditions to promote freezing is an attractive process for the treatment of produced water in areas where natural climatic conditions will seasonally promote freezing. The climates of New Mexico's San Juan Basin as well as the oil and gas producing regions of Colorado, Wyoming, and North Dakota are suited for application of this process.

A more economic and effective method for disposing and treating produced waters is obtained by coupling natural freezing and thawing processes with evaporation, which allows produced water to be dealt with throughout the year. The freeze-thaw/evaporation (FTE) process utilizes water treatment by freeze-thaw cycling during the winter months, when evaporation is ineffective, and water disposal by evaporation during the summer months. The coupling of freeze-thaw cycling with evaporation is easily achieved and allows natural conditions to be used to purify or dispose of produced water on a continuous basis. The FTE process is conducted using the same equipment required for evaporation, and switching from evaporation to freezing can be done simply by monitoring the ambient temperature. Further, purified waters from the melting ice can be separated from waters with concentrated constituent values created during the freezing process.

In 1992, personnel of B.C. Technologies, Ltd. (BCT) and the University of North Dakota's Energy and Environmental Research Center (EERC) began a research program with the objective of commercially developing the FTE process. This research, sponsored by Amoco Production Company, the US Department of Energy (DOE), and Gas Research Institute (GRI), is being conducted to evaluate the effectiveness of the natural FTE process as a water treatment technology. Specifically, the objectives of this research are to develop a commercial

FTE process for the treatment and purification of water produced in conjunction with oil and natural gas. The research required for development of this process consists of three tasks: 1) a literature survey, process modeling, and economic analysis; 2) laboratory-scale process evaluation; and 3) field demonstration of the process.

FTE PROCESS DESIGN

A flow diagram of the FTE process is presented in Figure 1. Produced water is placed in a holding pond. When the ambient temperature drops below 32°F, the stored water is sprayed onto a freezing pad to create an ice pile. A brine with elevated TDS concentrations drains from the freezing pad when the ambient temperature is below 32°F. Conversely, when the ambient temperature is greater than 32°F, ice on the freezing pad melts and purified water, with reduced concentrations of constituents, drains from the pad. A conductivity meter is used to readily identify the brine and purified water. The brine is disposed of by conventional methods and the purified water is stored for later beneficial use or is discharged. The FTE facility operation in summer involves exclusive use of evaporation; operation in winter, spring, and fall requires cycling of evaporation and freezing.

RESULTS OF INITIAL FTE PROCESS RESEARCH

A literature survey, environmental regulatory assessment, survey of current disposal practices and economics, and numerical process and economic modeling were completed in previous phases of the research. Project research began with a review of previous research related to water purification processes using both artificially induced and naturally occurring freezing for constituent removal. The compositions of typical oil and gas produced waters suitable for treatment by the FTE process and the typical range of meteorologic conditions where the process is applicable for treating produced waters were then determined. Next, process and environmental regulatory constraints were evaluated and a preliminary process design was completed. Numerical process and economic models were developed for the evaluation, and preliminary economic feasibility and sensitivity analyses based upon water composition, meteorological conditions, and facility design were conducted. Economic analyses were conducted to assess the commercial economic feasibility of the process and identify future research issues.

Twenty one laboratory-scale process simulations were completed in the second phase of the research, the FTE process economics were re-evaluated using the numerical process and economic models developed previously, and the results of the laboratory-scale process simulations conducted. An initial series of nine simulations to optimize the process design were completed. The impacts of produced water quality and climatic conditions were then investigated by conducting nine simulations in which three produced waters of different quality were treated under three differing sets of atmospheric conditions. Finally, a duplicate simulation using each produced water was conducted and the experimental products of these simulations were subjected to detailed organic, inorganic, and radionuclide analyses. The detailed analytical results were used to determine the effectiveness of the process in removing organic, metal, and salt constituents from produced waters.

The following conclusions were drawn based upon the predemonstration results of this research:

- Freeze-crystallization is effective in removing a wide variety of constituent mixtures from water. The process is capable of simultaneously removing salts, organics, and heavy metals (including NORM) from produced waters.
- Regulatory and permitting requirements and associated costs for an FTE facility are essentially the same as those of conventional evaporation facilities.
- The FTE process can provide significant quantities of water of a quality suitable for various beneficial uses from oil and gas produced waters. Treated waters with TDS concentrations in the range of 200 to 1500 mg/l can be readily produced using the FTE process.
- The FTE process is commercially feasible in the Rocky Mountain and Great Plains Regions for treating 500 bbl/day or more of produced water. For a 1,000 bbl/day produced water treatment facility operating in these regions, the cost for produced water treatment/disposal is approximately $0.20 to $0.30/bbl.
- The FTE process is applicable, in most regions where subfreezing temperatures seasonally occur, to treat most waste waters containing mixtures of salts, organics, and/or heavy metals in concentrations below eutectic compositions. Potential applications of the process are: oil and gas produced waters, drilling fluids, refinery and gas treatment plant waste waters, groundwater decontamination, water desalinization, industrial waste waters, municipal waste waters, and contaminated waters associated with defense plants.

RESULTS OF THE FTE PROCESS DEMONSTRATION IN THE SAN JUAN BASIN OF NEW MEXICO

Results of the laboratory simulations completed previously confirm that the FTE process is capable of providing significant quantities of water, suitable for beneficial use, from oil and gas produced waters. In addition, the economic analyses using the simulation results continue to indicate that the process has significant commercial economic potential. For these reasons, a field demonstration of the FTE process was conducted to confirm the results of the laboratory-scale simulations at an operating field site. The demonstration of the FTE process was conducted to confirm: 1) the commercial-scale feasibility of the process, 2) the environmental acceptability of the process in order to facilitate regulatory permitting, and 3) the economic viability of the process in order to obtain investment capital. In addition to the objectives listed above, the field demonstration was conducted to provide data to: 1) accurately design and project the economics of commercial-scale operation of the FTE process and 2) facilitate applications of the process to a variety of locations and produced waters.

Amoco Production Company's Cahn/Schneider evaporation facility was the site of the FTE process demonstration and personnel from Amoco's San Juan Operations Center obtained approval from the New Mexico Oil Conservation Division (OCD) to conduct the demonstration project. This conventional evaporation facility is located 22 miles south of Durango, CO and 43 miles north of Farmington, NM. Based upon discussions with New Mexico OCD personnel, it was agreed that the FTE demonstration plant would attempt to treat 20,000 bbl of produced water during the winter of 1995-96 and that all products of the demonstration, including treated water generated, would be disposed of by conventional methods. Produced water was trucked to the facility from nearby coal bed methane wells.

The original layout of the FTE demonstration plant constructed in the fall of 1995 at the Cahn/Schneider facility is provided in Figure 2. The Schneider evaporation pond is approximately 2 acres in size and was to serve as the produced water holding pond and final repository of the demonstration products. A feed pump, automatic controls, and a 2500 ft long above ground feed line to the Cahn pond were installed and insulated to transfer water from the Schneider pond to the Cahn pond. The Cahn evaporation pond is one acre in size and was prepared as the freezing pad. A one-and-one-half foot internal-berm was constructed of sand bags

to isolate a portion of the Cahn pond as the freezing pad. The Cahn pond was approximately six times the size required to achieve the project objective of treating 20,000 bbl. The required piping, controls, and a tank farm were installed to separate runoff from the freezing pad. Fluids stored in the tank farm would then be re-introduced into the Schneider pond after sampling and analysis.

Shakedown of the FTE demonstration plant was conducted in late November and early December 1995. During the shakedown, it was found that the water in the Schneider pond had a TDS concentration of 120,000 ppm resulting from solids accumulated in the pond prior to filling. The decision was made to modify the plant operation so that a representative coal bed methane produced water could be treated. Since the Schneider pond was not useable as the produced water holding pond, demonstration operation during the winter of 1995-96 was restricted to using only the Cahn pond. As a result of this decision, the Cahn pond now became effectively the produced/recycle water holding pond and the freezing pad (Figure 2). The modification made it possible to test the ability of freeze-crystallization to effectively treat coal bed methane produced water, but prohibited a demonstration of the design improvements made in the FTE process compared to the natural freezing processes tested over three decades ago. Integral to the FTE process operation is the ability to evacuate runoff from the freezing pad so that the ice pile created can effectively drain and that the runoff be separated into treated water, intermediate (recycle) water, and brine. Since water could no longer be recycled to the Schneider pond, the intermediate process stream had to remain in the Cahn pond. Thus, the ability to capitalize on the dynamic freeze/thaw cycling that occurs as a result of the prevailing climatic conditions in the San Juan Basin of New Mexico was lost due to the loss of process stream separation capability. This had a major impact on plant operations. Another complication was that the produced water supply was severely limited due to the inability to use the produced water in the Schneider pond. Instead of having the ability to feed the Cahn pond with fresh feed when needed, operations were now, at times, limited by both the quantity of produced water that could be delivered and the need to empty the feed tanks when water delivery was possible.

Operation of the modified demonstration plant was initiated in December 1995 and was terminated in March 1996. Originally, the demonstration plant was scheduled to run through the spring and summer of 1996 to obtain evaporative data for the evaluation. Instead, GRI requested the plant be idled during the summer of 1996

and operation of the FTE demonstration plant resume in October 1996 and continue operation through the summer of 1997.

The winter of 1995-96 was one of the warmest winters in the San Juan Basin in the past 25 years. Historical temperature data for Farmington, New Mexico reveals that every month from November 1995 through March 1996 were much warmer than typical. The warm temperatures occurring in November and early December did not impact the FTE demonstration. The warm temperatures occurring from December 9 through December 21, 1995 did limit operation of the demonstration significantly. Even though January 1996 was warmer than usual, temperatures were sufficiently cold to allow for operation of the demonstration during most of the month and a significant ice pile was created. February, however, exhibited much warmer average temperatures than typical and the unusually warm temperatures severely impacted the operation of the FTE process demonstration.

On 2/1/96 composite samples of feed water, ice, and brine were collected and submitted for detailed chemical analyses. The feed and brine samples were composited over the time period from 12/9/95 to 2/1/96. The composite sample of the ice pile was collected on 2/1/96. The results of the detailed analyses of the 2/1/96 composite samples of feed, ice, and Cahn pond recycle water indicate:

- Melt produced from the ice would be suitable for various beneficial uses.
- The TDS concentration in the ice produced was reduced by 92% and the TDS concentration in the brine was increased 390% compared to that of the feed.
- The concentrations of all inorganic constituents analyzed were significantly reduced in the ice produced and the concentrations of most inorganic analytes were significantly increased in the brine compared to their respective concentrations in the produced water feed.
- No volatile organics were detected in the ice produced in concentrations above the EPA Estimated Quantitation Limit (EQL).
- No semi-volatile organics were detected in the ice produced in concentrations above the EPA EQL.

As discussed in previous sections, the modifications of the FTE demonstration plant design, coupled with the unusually warm February at the site, prevented the harvest of treated water from the ice melt. However, the operating data collected and the results of analyses of the 2/1/96 sampling can be used to determine how the demonstration would have performed, if the capability had existed to pump all the brine from

the Cahn pond during the operation. At the time of sampling, 10,038 bbl of produced water had been fed to the Cahn pond. Three days prior (1/29/96) to the sampling the decision was made to transfer brine to the Schneider pond because of the high TDS concentration of the unfrozen water in the Cahn pond. The brine transferred had a TDS concentration of 56,900 ppm. However, it was not possible to transfer a substantial portion of this brine to the Schneider pond as the feed tanks were full, which necessitated that the brine be transferred using the Cahn pond transfer pump. This pump is designed for low-head applications, and the pressure drop in the 2500 ft line from the Cahn pond to the Schneider pond, coupled with the 20 to 30 foot elevation increase, limited pump performance to 20 gpm. For these reasons, it was possible to transfer only 341 bbl of the approximately 2000 bbl of brine in the pond at that time, making it impossible to harvest the ice melt. Since February 1996 was the warmest February recorded since 1968, it was not possible to re-concentrate the water in the Cahn pond.

A TDS balance for the time period of 12/9/95 to 2/1/96 allows the demonstration performance to be estimated with reasonable accuracy. The assumption that evaporation occurring during this time period was negligible is required. This assumption is reasonable since the pond was covered with ice during most of that time period. The results of the TDS balance examination indicate that approximately 8100 bbl of treated water could have been produced from the ice melt and 1900 bbl of brine would have required further treatment or disposal. The reduction in the required disposal volume is 81% and a treated water to brine yield is approximately 4-to-1 (Table 1).

Realizing that the modifications required to operate the FTE demonstration during the winter of 1995-96 negated most of the advantages of the FTE process over historical natural freeze-crystallization processes, and that the exceptionally warm winter compounded the operating difficulties, the organizations funding the demonstration were encouraged by these limited results and have agreed to fund another year of FTE demonstration plant operation. In addition, a new, more economic, and environmentally safe evaporation pond design will also be tested this year. This design will significantly reduce the capital requirements necessary to conduct the FTE process. In summary, the first year of the FTE demonstration was a limited success.

The FTE economic model was used to estimate the commercial-scale economics of an FTE plant treating coal bed methane waters in the San Juan Basin of New Mexico.

Considering a FTE facility treating an annual average of 1,000 bbl/day of produced water, operating with treated water and brine yields similar to those determined from the demonstration TDS balance, the cost per bbl of treated water produced would be in the range of $0.20 to $0.30. When the significant evaporation rates in the basin are considered, the cost per bbl of produced water treated or disposed of is <$0.20. However, these economic projections do not consider the costs of produced water transportation or brine disposal.

The post-demonstration economic analyses of the FTE process continue to indicate favorable commercial-scale economics. However, personal communication with oil and gas industry personnel suggest that the cost of transportation of produced water to the FTE facility continues to be very expensive and would limit the use of the Cahn/Schneider facility to a reduced capacity. As a part of next year's FTE demonstration project research, the feasibility of one operator running multiple smaller FTE facilities at the wellhead will be investigated. If feasible, the FTE process could be utilized in the San Juan Basin to dramatically reduce produced water transportation costs which are currently greater than the disposal cost in this and many other areas.

CONCLUSIONS

The following conclusions regarding the technical and economic feasibility of the FTE process are drawn based upon the results of the research conducted:

- The FTE process is capable of economically providing significant quantities of water of a quality suitable for beneficial use from oil and gas produced waters. Treated waters with TDS concentrations in the range of 200 to 1500 mg/l can be readily produced using the FTE process. Results of sample analyses indicate that organics and metals are also significantly removed.
- This research confirms the FTE process is commercially feasible in the Rocky Mountain and Great Plains Regions treating 500 bbl/day or more of produced water. For a 1,000 bbl/day produced water treatment facility operating in these regions, the cost for produced water treatment/disposal is $0.25/bbl.
- This research and previous research confirms freeze-crystallization is effective in removing a wide variety of constituents from water. This process is capable of simultaneously removing salts, organics, and heavy metals (including NORM) from produced waters.
- Regulatory and permitting requirements for an FTE facility are similar to those of conventional evaporative disposal methods for produced waters.

- The FTE process is applicable, in regions where sub-freezing temperatures seasonally occur, to treat most waste waters containing mixtures of salts, organics, and/or heavy metals in concentrations below eutectic compositions. Potential applications of the process are: oil and gas produced waters, drilling fluids, refinery and gas treatment plant waste waters, groundwater decontamination, groundwater desalinization, industrial waste waters, municipal waste waters, and contaminated waters associated with defense plants.
- An on-site demonstration of the FTE process was completed in the San Juan Basin of New Mexico treating produced water from numerous coal bed methane wells.

Commercial impact from this project research is expected in 1998 as a result of the continuing demonstration project. The potential impact of this research is:

- Increased production from depleted and/or marginally economic oil and gas reserves.
- Reduced operating expenses for reserves that are currently economic.
- Development of new coal bed methane reserves.
- Reduced costs of pump and treat groundwater cleanup.
- Reduced treatment cost for industrial waste water.
- Facilitation of sustainable municipal and agricultural development in the arid western US.
- Reduced costs for decommissioning defense plants.

Due to the limitations of this paper, the reader is referred to the literature for detailed discussions of the results of this research program (1).

REFERENCES

1. Boysen, J.E., K.L. Walker, J.L. Mefford, J.R. Kirsch, and J.A. Harju, "Evaluation of the Freeze-Thaw/Evaporation Process for the Treatment of Produced Waters - Final Report," US DOE, August 1996, in press.

Table 1.
FTE Demonstration TDS Balance Results Summary

	Produced Water Feed	Brine	Ice
TDS, ppm	11,600	56,900	940
Volume, bbl	10,038	1,912	8,126
Yield, % of feed		19%	81%

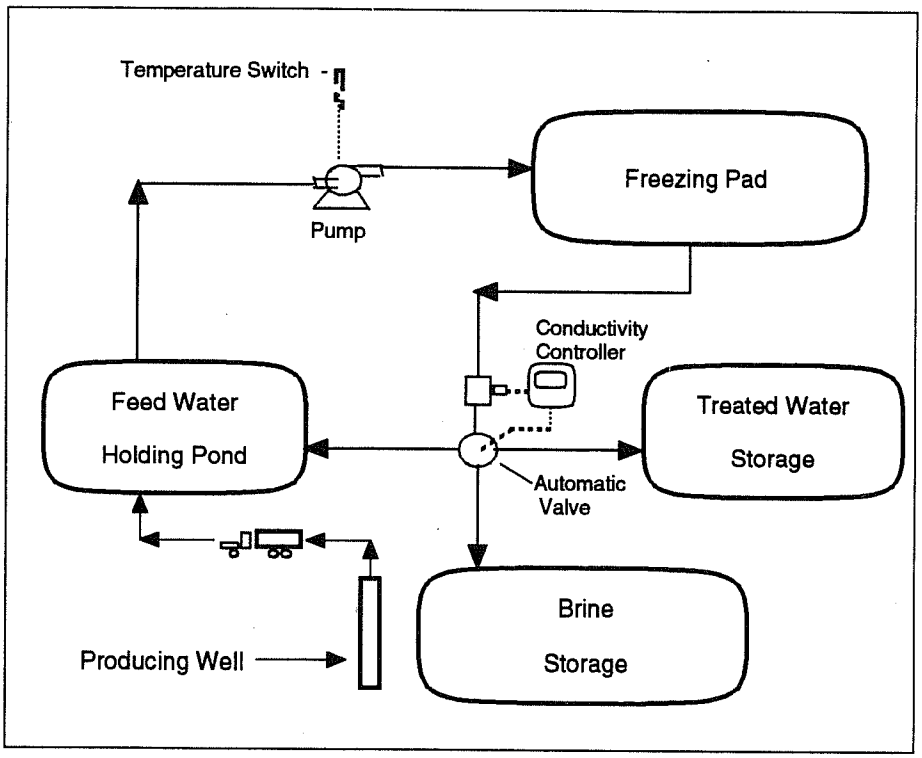

Figure 1. Block flow diagram of the FTE process.

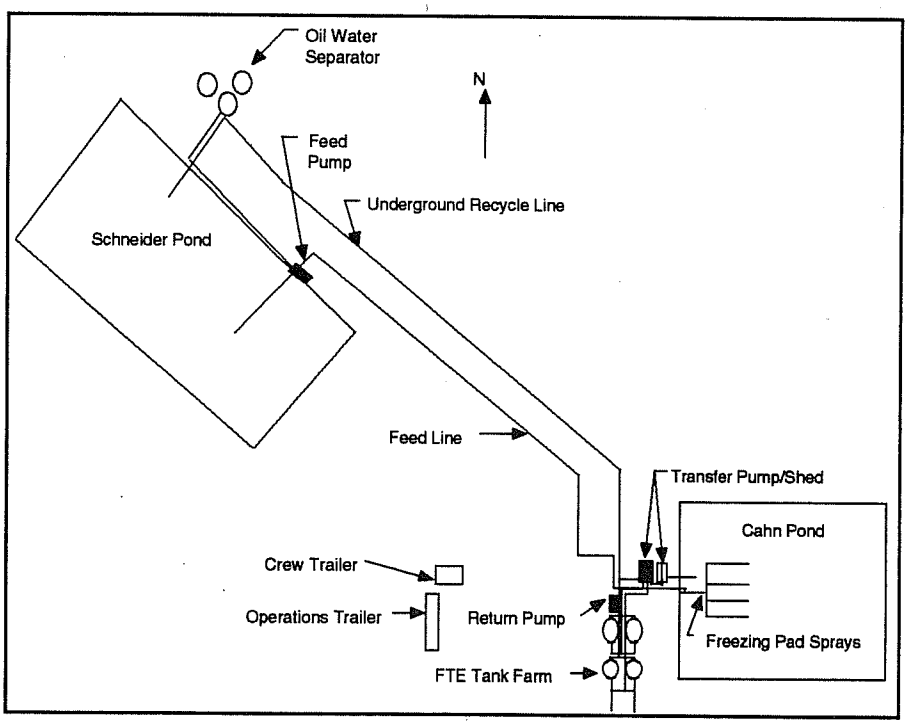

Figure 2. FTE Demonstration Site Layout

Demonstration of Produced Water Treatment for Direct Discharge

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The biological granular activated carbon-fluidized bed reactor (GAC-FBR) process is a high rate treatment system for economically degrading water soluble organics, such as benzene, BTEX, oil and grease (O&G) and organic acids, at high rates and short residence times. In many instances, removal of water soluble organics, after deoiling, is sufficient for meeting discharge requirements. At other sites, a reduction in the TDS concentration will be necessary prior to meeting surface discharge requirements. Results of a field demonstration (up to 350 barrels per day) where a treatment train consisting of deoiling, removal of water soluble organics using the GAC-FBR were coupled to a bench-scale electrodialysis (ED) unit for TDS removal, are presented.

Consistent removal of organics was observed even during periods when the up-front deoiling was not operating properly. Effluent O&G of less than 5 mg/L was consistently measured; most organics (i.e., BTEX, acetate) were removed to below drinking water standards.

Based on the results obtained, costs for organics removal (deoiling followed by the GAC-FBR for water soluble organics removal) were estimated for 4000 barrels per day of produced water. The total cost, including 10-year amortization of capital, was estimated to be $0.068 per barrel. O&M costs alone ranged from $0.02-0.04 per barrel.

Demonstration of Produced Water Treatment for Direct Discharge

Introduction

The Granular Activated Carbon-Fluidized Bed Reactor (GAC-FBR) process is a high-rate system for performing biological treatment of low to moderate strength wastewaters and process effluents. The process is particularly well suited for removing dissolved organics at high applied organic loading rates (OLR) and short retention times (minutes). The process has been successfully used at full scale for treatment of a number of applications including wastewaters from chemical plants, refiners, bulk storage terminals, municipal wastewaters. The process can be operated as an aerobic, anoxic (denitrifying) or anaerobic system. The use of an adsorptive biomass carrier in the form of granular activated carbon (GAC) affords the process robustness during adverse environmental conditions beyond that possible with other biological fixed film systems. This makes the process an ideal candidate for treating produced waters which can be highly variable in nature.

Background

A demonstration of produced water treatment using a commercial-scale biological GAC-FBR system was conducted in Lysite, Wyoming. The object of this demonstration was to evaluate the feasibility of a treatment train which provided 1) consistent reduction of oil and grease (O&G) and water soluble organics to a level acceptable for surface discharge and 2) determine if this effluent could be effectively demineralized. A schematic of the treatment train used at the site is depicted in Figure 1. The order of treatment was as follows: 1) Induced Gas Flotation (IGF) for deoiling; 2) sequential anoxic and aerobic GAC-FBRs for removal of residual O&G and water soluble organics; and 3) electrodialysis (ED) for demineralization. Only the work pertaining to removal of organics will be presented herein.

The IGF unit was installed to remove colloidal and suspended O&G. The Wyoming permit O&G discharge limit is 10 mg/L. EPA 413.1 (Freon extraction method), however, measures soluble compounds which are not removed by conventional deoiling. Therefore, removal of dissolved organics was necessary to achieve O&G limitations as well as reducing the potential for membrane fouling on the ED unit due to biological growth due to the relatively high concentration of dissolved organics.

The deoiling process consisted of polymer addition followed by the IGF unit (injection of 40 micron air bubbles). Following deoiling by the IGF, a two-stage GAC-FBR was used for removal of soluble organics. The produced water at the Lysite, WY site had a relatively high concentration of volatile fatty acids, and other hydrocarbons typically associated with produced waters (Table 1). Pilot-scale treatability studies, performed previously indicated that a two-stage GAC-FBR (anoxic followed by aerobic) might be a cost effective treatment option for treatment of organics in the produced water. The first stage for this process (anoxic) was designed to remove the bulk of influent soluble organics, including acetate, some aliphatic and potentially, some aromatic compounds at relatively high organic loading rates (40 kg COD/m^3-d); the second stage (aerobic) was designed to remove remaining hydrocarbons and other water soluble (dissolved) organics. High OLRs are possible with an anoxic GAC-FBR because dissolution of oxygen, the rate limiting step for the aerobic system, is not required. Sodium nitrate (ca. 100 mg/L) was added as the electron acceptor (in place of oxygen) for the anoxic system.

This two-stage system was successfully used at the laboratory-pilot scale using water from this site. A characterization of the water is provided in Table 2. Virtually complete removal of all water soluble (dissolved) organics was achieved.

Start-up

Start-up and inoculation of the two GAC-FBR systems was completed on November 11, 1995. Both reactors were inoculated with approximately 10 gallons of "seeded" GAC (GAC having an established biofilm with acclimated microorganisms attached). Both the aerobic and anoxic systems were fed directly with effluent from the IGF for the first month of operation. This ensured adequate "food" was available to hasten development of mature biofilms in both reactors. High removal efficiency for all hydrocarbons was achieved. Effluent quality during this start-up period was good for both systems. A maximum benzene concentration of 25 µg/L was observed in the anoxic GAC-FBR after 40 days operation. Benzene was consistently below detection (<1 µg/L) in the effluent from the aerobic GAC-FBR.

Results

Deoiling System Performance

Approximately 1.3 million gallons of produced water were treated for organics removal over 65 days of operation, and approximately 2000 gallons of

float material was removed from the IGF unit. The float material consisted of O&G, suspended solids, and some water. Samples of the float materials had a moisture content of 0.6%.

The O&G concentration in the IGF achieved the permit requirement of 10 mg/L or less on only seven sampling events. Average influent O&G was 71 mg/L, while the average effluent concentration was 53 mg/L. Composition of the effluent from the IGF for the entire project period (30 sample events) is presented in Table 1. Very little removal of BOD_5 and COD (average of 4% and 2%, respectively) was observed through the IGF unit. This is because most of the organics were dissolved in nature.

Overview of Operation of Anoxic and Aerobic GAC-FBRs

On December 12th, after both the anoxic and aerobic systems were observed to be sufficiently well seeded (i.e., mature biofilm had developed), the anoxic and aerobic GAC-FBRs were placed in series (sequential) operation. Effluent from the IGF was fed to the anoxic GAC-FBR which in turn fed directly to the aerobic GAC-FBR. When this switch was made, the anoxic GAC-FBR was removing approximately 91% of the influent acetate and much of the total volatile hydrocarbons (TVH). The oxygen demand placed on the aerobic system, therefore, was much lower than when fed directly from the IGF.

Several changes in HRT of both reactors were made over the 40 days of series operation. During this period, the HRT for the anoxic system was stepwise reduced from 23 to 18, and finally 13.5 minutes. The HRT in the aerobic GAC-FBR during this same period was reduced from an original HRT of 94 minutes, to 38, then to 23 minutes. Performance of the GAC-FBRs is described below. The final effluent from the series operation was consistently of high quality with low concentration of O&G, benzene and all dissolved organics achieved.

Performance of the Anoxic GAC-FBR

The performance of the anoxic GAC-FBR at each of the conditions tested was good. As expected, the removal of benzene, xylenes and some of the TVHs was initially high, but decreased as the adsorptive capacity of the GAC carrier particles became saturated. Near the end of the demonstration, when the concentration of benzene with influent decreased, effluent benzene concentrations from the anoxic GAC-FBR were approximately equal to and sometimes slightly exceeded the influent concentration (Figure 2). Toluene removal in the anoxic GAC-FBR, however, increased over this same period (Figure 3). It can be

inferred from these observations that toluene and other volatile hydrocarbons are degraded at high rates under anoxic conditions (Figure 4).

The ability of the anoxic GAC-FBR to achieve high mass removal provided a modulating effect on the concentrations of BTEX and TVH introduced to the aerobic GAC-FBR. As can be seen in Figure 5, spikes in the TVH concentrations entering into the anoxic GAC-FBR were significantly dampened allowing for a much more consistent applied OLR to the aerobic system. The result was consistently high removal of O&G, benzene, and all dissolved organics.

Effluent concentrations of acetate were below detection during each of the five operational periods. The COD concentration in the effluent remained low, with the exception of four occasions, two of which were during occurrences where large quantities of the oil entered the treatment system. The anoxic GAC-FBR removed on average, 50 to 75% of the applied COD (588 mg/L) at HRTs of 13 to 18 minutes and OLR up to 46 Kg COD/m^3-d.

Performance of the Aerobic GAC-FBR

OLRs of 1.9 to 16.1 Kg COD/m^3-d were applied to the aerobic GAC-FBR over the 40 days of series operation.

Effluent from the aerobic GAC-FBR had an average O&G of 4.3 mg/L and a median value of 3.0 mg/L (Figure 6). Average removal efficiency for O&G was 94.3%. The only time the effluent O&G exceeded the 10 mg/L limit was on an occasion when free oil was passed from the IGF into the FBRs. The effluent O&G from the FBR system was 12 mg/L during that day. Overall removal of BTEX in the aerobic GAC-FBR was high, 98 to 99.9%; effluent benzene concentration was consistently below detection limits (1 µg/L). In Figure 4, a chromatogram from the analysis of volatile compounds up to C15, the high quality of the effluent discharged from the aerobic reactor is presented; only traces of volatile hydrocarbons were observed.

Changes in OLR did not significantly affect the quality of the effluent, as long as sufficient dissolved oxygen was available. The aerobic GAC-FBR was operated at a maximum OLR of approximately 16 Kg COD/m^3-d during a 3-day period (1/18-1/20/96). During this period, oxygen dissolution was the limiting factor, the effluent DO could not be maintained at the setpoint of 2 mg/L. Even with this limitation, 93.7% removal of the TVH and >99.9% of the benzene was achieved. During the final two operational periods, effluent O&G was below the 10 mg/L limit, averaging 6 mg/L. The aerobic GAC-FBR was operated at an HRT of 23.4 minutes, the lowest used during this demonstration. These two periods differed greatly in the overall applied OLR to the two-stage GAC-FBR

system, 16.1 and 7.0 Kg COD/m^3-d, respectively. There was a large influx of oil into the treatment system on 1/18/96. This resulted in increased concentrations of TVH, oil and grease, and COD fed into the aerobic GAC-FBR for several days. Effluent quality from the aerobic GAC-FBR during this operational period was comparable to that observed when the OLR was lower (Tables 3 and 4). During large fluctuations in OLR, removal efficiency of the aerobic system was consistently good.

Economics of Organics Removal

An economic analysis was performed based on a design that would be able to treat 4000 barrels per day of produced water. The design was based on being able to consistently provide adequate treatment at the 95 percentile conditions observed during the demonstration period at Lysite, WY.

Economic analysis of the biological treatment process (GAC-FBR) utilized at the Lysite site suggests that a single-stage aerobic system would be the most cost effective alternative. Despite the fact that the anoxic system performed well technically, the high cost of shipping sodium nitrate to the site reduced the economic attractiveness of this process option. Operating costs were calculated to be $0.02 per barrel for the single-stage aerobic system compared to just over $0.04 per barrel for the two-stage system. Overall costs of the single-stage aerobic system, including capital was estimated to be $0.068 per barrel for the 4000 barrel per day system.

Conclusions

Removal of O&G and other water soluble organics was achieved on a consistent basis. The NPDES "beneficial use" permit requirements for O&G were consistently met. The O&G concentration exceeded 10 mg/L on one instance and this was associated with free oils escaping from the IGF and entering the biological treatment system. Meeting the O&G discharge requirements was not attainable with the IGF system alone. Effluent discharged from the coupled anoxic/aerobic GAC-FBRs was of high quality containing less than 1 µg/L benzene and low concentrations of all water soluble organics. No biological or other fouling of the membranes for the pilot ED unit was observed.

The GAC-FBR based treatment system appears to be quite economical. Total cost of treating 4000 barrels per day including capital was estimated to be $0.068 per barrel.

Table 1
Average Composition of the Produced Water after Deoiling for the Entire Study Period

Constituent	Mean	Median
Benzene (µg/L)	3,620	3,100
BTEX (µg/L)	17,710	16,750
TVH (µg/L)	63,750	49,840
DNPOC (mg/L)	140	170
Acetate (mg/L)	171	175
COD (mg/L)	588	--
O&G	53	29

Table 2
Characterization of Lysite, WY Onshore Water from Samples taken on 6/27/96.

Conventional Parameters	
Specific conductance (µmhos/cm)	11800
Total dissolved solids (mg/L)	8340
Total suspended solids (mg/L)	122
Fixed suspended solids (mg/L)	100
Volatile suspended solids (mg/L)	22
Chloride (mg/L)	3710
Sulfate (mg/L)	5.9
Sulfide (mg/L)	8.7
Oil and grease (µg/L)	53.4
pH (s.u.)	6.8
Total recoverable petroleum	119
Hydrocarbons (mg/L)	119
Total alkalinity (mg/L)	996
Alkalinity, carbonate (mg/L)	0
Alkalinity, bicarbonate (mg/L)	996
TOC (mg/L)	211
Fluoride (mg/L)	2.3
Iron (mg/L)	9.4

Table 3

Performance of Coupled Anoxic/Aerobic GAC-FBR in Series Operation - Period 4.

Components	IGF Effluent	Anoxic Effluent	Aerobic Effluent	Overall Removal (%)
Benzene (µg/L)	1,464	1,731	<1	>99.9
Toluene (µg/L)	4,748	380	7	99.9
Xylenes (µg/L)	6,652	1,985	59	99.1
BTEX (µg/L)	12,863	410	67	99.5
TVH[1] (µg/L)	63,495	22,533	2,618	95.9
DNPOC[2] (mg/L)	103	37	27	73.8
Acetate (mg/L)	123	<2	<2	>98.4
Oil & Grease[3] (mg/L)	72	NA	3	95.8
Operating Conditions		**Anoxic GAC-FBR**	**Aerobic GAC-FBR**	**Overall**
Flow Rate (gpm)		10.5	5.0	
Applied COD[4] (mg/L)		508	195	508
Removed COD[4] (mg/L)		313	111	424
ΔDO/ΔCOD			1.25	
Applied OLR[4] (Kg COD/m^3·d)		39.7	7.5	12.8
HRT (minutes)		17.9	37.6	55.5

[1]TVH - Total Volatile Hydrocarbons - as measured via headspace GC-FID.
[2]DNPOC - Dissolved, Non-Purgable Organic Carbon.
[3]Data supplied by ReTec.
[4]Calculated COD values based on summation of TVH, acetate and DNPOC (less contribution of acetate).

Table 4

Performance of Coupled Anoxic/Aerobic GAC-FBR in Series Operation - Period 5.

Components	IGF Effluent	Anoxic Effluent	Aerobic Effluent	Overall Removal (%)
Benzene (µg/L)	1,722	1,770	<1	>99.9
Toluene (µg/L)	3,048	227	14	99.5
Xylenes (µg/L)	2,965	1,873	137	95.4
BTEX (µg/L)	7,735	3,870	151	98.0
TVH[1] (µg/L)	19,424	10,775	3,078	84.2
DNPOC[2] (mg/L)	118	23	23	80.5
Acetate (mg/L)	148	<2	<2	>98.6
Oil & Grease[3] (mg/L)	17	NA	4	76.5
Operating Conditions		**Anoxic GAC-FBR**	**Aerobic GAC-FBR**	**Overall**
Flow Rate (gpm)		14.0	8.0	
Applied COD[4] (mg/L)		422	114	422
Removed COD[4] (mg/L)		307	47	354
ΔDO/ΔCOD			2.47	
Applied OLR[4] (Kg COD/m^3·d)		46.1	7.0	16.8
HRT (minutes)		13.4	23.4	36.8

[1]TVH - Total Volatile Hydrocarbons - as measured via headspace GC-FID.
[2]DNPOC - Dissolved, Non-Purgable Organic Carbon.
[3]Data supplied by ReTec.
[4]Calculated COD values based on summation of TVH, acetate and DNPOC (less contribution of acetate).

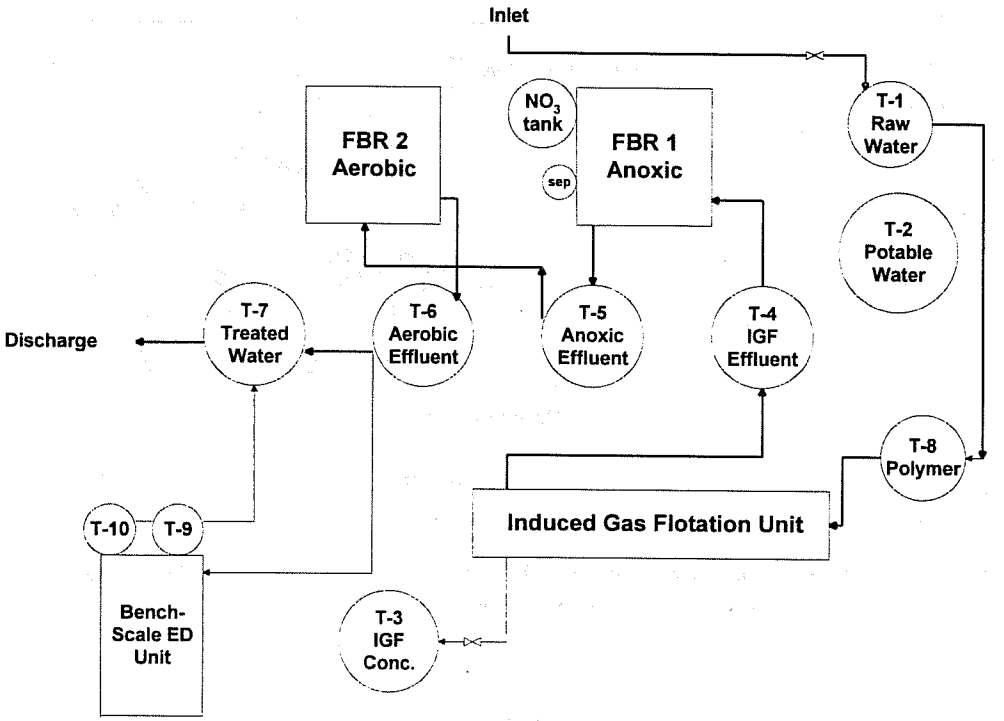


Figure 1. Schematic of Process for Produced Water Treatment in Lysite, WY.

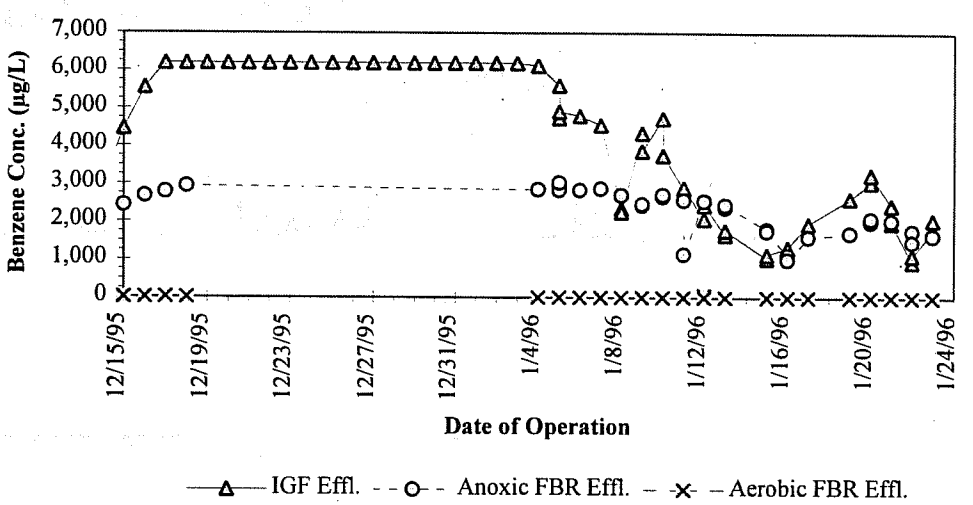


Figure 2. Effluent Benzene Concentration from the Anoxic and Aerobic GAC-FBRs during Series Operation.

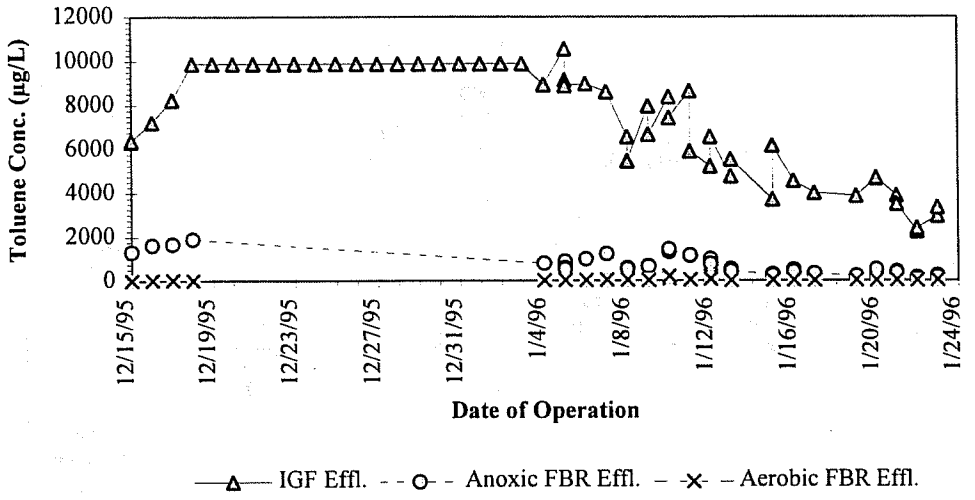


Figure 3. Effluent Toluene Concentration from the Anoxic and Aerobic GAC-FBRs during Series Operation.

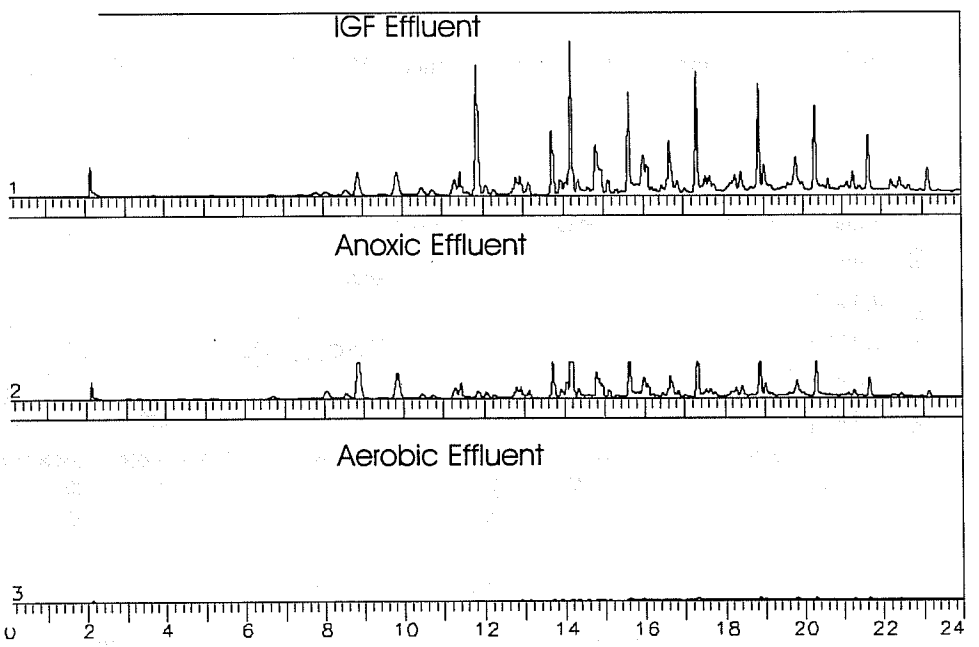


Figure 4. Chromatogram Showing TVH Concentrations of the Effluents from the IGF (a), Anoxic (b) and Aerobic GAC-FBR (c).

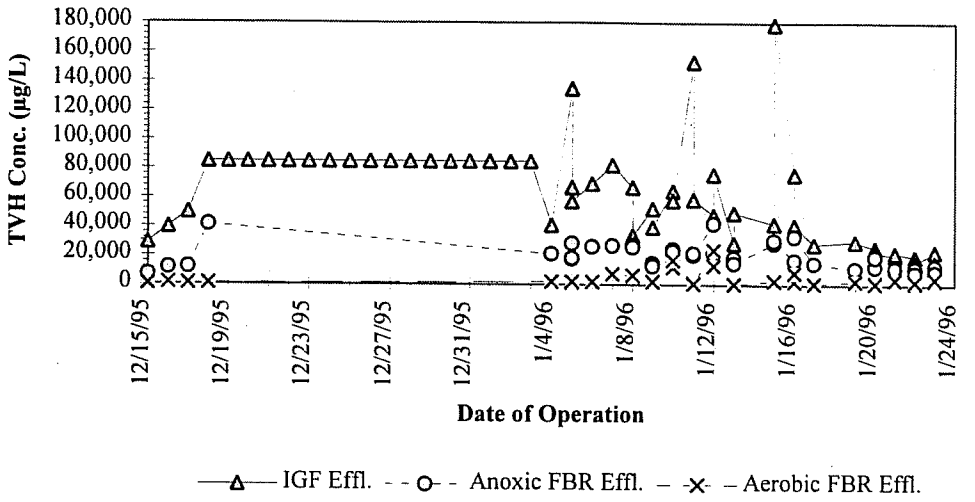


Figure 5. Effluent TVH Concentration from the Anoxic and Aerobic GAC-FBRs during Series Operation.

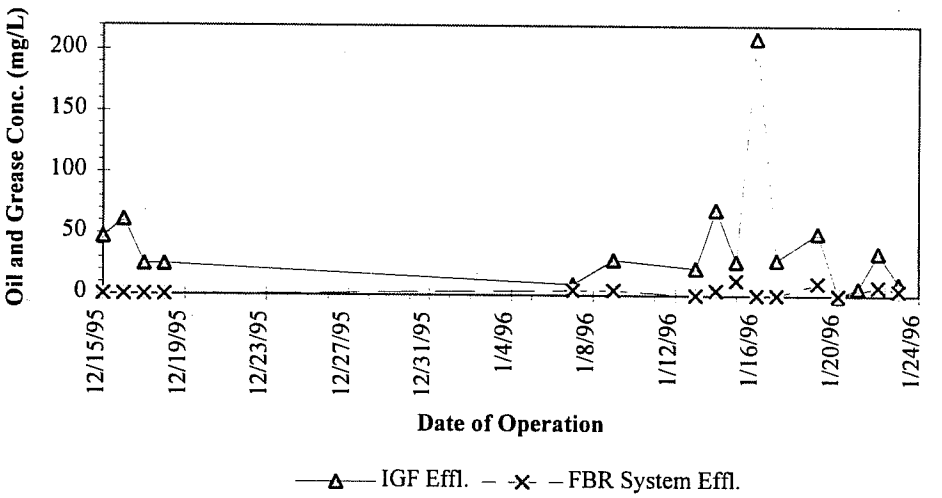
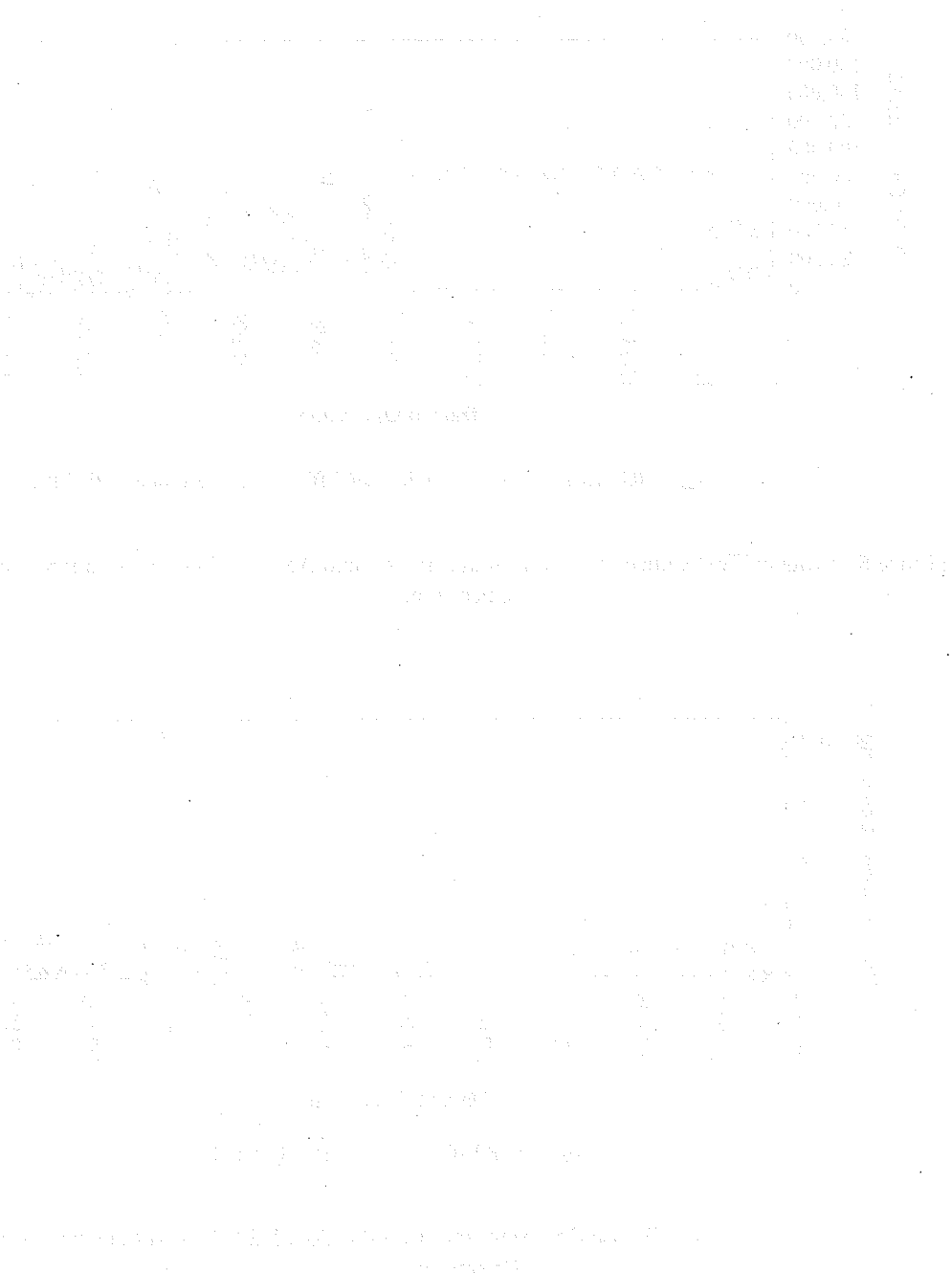


Figure 6. Effluent Oil and Grease Concentration from the Coupled GAC-FBRs during Series Operation.



Wastewater Treatment Using Electrochemical Systems

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Abstract:

Elemental hydrogen,H_2, and oxygen, O_2, gases are produced by water electrolysis using low direct current, DC, potentials. Steel plates are used as anode and cathode electrodes in this process. Fine diffused bubbles are generated during the electrolysis. These bubbles tend to coalesce around the suspended solids in wastewater. At the same time, the buoyant effect of the gases creates a mild agitation in the electrolytic cells. This agitation is conducive to flocculation within the cell. Oxidation of the anode results in the formation of ferrous iron in the cell. The dissolved iron enhances the coagulation of the suspended solids in the wastewater. The combined effects of bubble coalition, mixing and iron coagulation emulate the results obtained in conventional dissolved air flotation, DAF, systems where iron salts are used as coagulants. Coagulated solids are then removed as scum from the surface of the reactor. Opposite DAF, electrolytic systems have no moving parts and can be operated under atmospheric conditions.

Removal efficiencies of biochemical oxygen demand, BOD_5, and total suspended solids, TSS were evaluated in a 36.5 L (10 gal) electrolytic reactor. The degree of agitation, flotation and chemical coagulation in the reactor were controlled by varying the applied potential, the separation of the electrodes and the treatment time. Electrode spacing varied from 1.8 to 7.5 cm. Applied voltages varied from 3.0 to 9.0 V. Low efficiencies were observed under low and high applied power conditions. Optimal removal occurred in the intermediate applied power range, where close to 60% of both TSS and BOD_5 was achieved at 2.3 KW-Hr/m^3 in approximately 100 min treatment time. Optimal electrode spacing and potential in this case are 5.5 cm and 6.0 V respectively.

Electrolytic methods for wastewater treatment date back to the advent to the twentieth century. For example, an electrolytic treatment of waste was patented by W. Webster in 1889 (US Patent No. 398,101, 1889). According to this patent, the wastewater were electrolyzed with iron electrodes at a potential of about 10 V. Seawater or salt was added to the wastewater if insufficient chlorides were present to generate chlorine. Iron electrodes were specified to take advantage of the formation of hydrated iron oxides, which aided in sludge flocculation. An electrolytic wastewater treatment plant was built at Crossness, a suburb of London, England (Miller and Knipe, 1965).

Another early patent was granted to J. T. Harris on the use of water electrolysis for wastewater treatment (US Patent 937,210, 1909). His concept was based on the use of both aluminum and iron electrodes. A small copper electrode was also used in this patent as a disinfection agent. The patent claims better coagulation and metal removal using these electrodes simultaneously than previously reported results for single-metal electrode systems.

The use of electrolytic methods for wastewater treatment gained momentum in the earlier part of this century. Plants based on this principle were built in Santa Monica, California and Oklahoma City, Oklahoma between 1910 and 1920 (Miller and Knipe, 1965). The wastewater flowed through steel plates separated about 1/2 inch. Paddles were moved between the spaces to remove scum and to insure mixing of the solution. Lime was added to increase the solution pH and to minimize electrode corrosion. These processes were extremely fast, with contact times in the electrolytic chamber of about 1.0 minute. Solids were separated in a final clarifier. Effluent was described as clear, odorless and non-putrescent. Reports from other plants built around the same time are equally favorable (Miller and Knipe, 1965).

The short residence time in the electrolytic process allowed the plants to be built in areas where land was at a premium. These factors were decisive in the selection of electrolytic systems for wastewater treatment at Elmhurst, New York and Allentown, Pennsylvania. All municipal wastewater treatment plants that operated using this principle in the United States were abandoned by the early 1930's. The trend at that time was to replace these plants for more economical primary treatment units, whose performance was enhanced by the addition of lime (Miller and Knipe, 1965).

Around this time, electrolytic units gained acceptance for the treatment of oily industrial wastes. A 7.0 MGD plant was built to enhance separation of oil from an industrial waste effluent (US Patent No. 1,746,964, 1930). Graphite anodes were used in this electrolytic process. The cathodes were made of steel. The process was very effective in removing oil and grease. The oil emulsion was coagulated and separated by flotation into hard, odorless layers. An early

patent also exists for the removal of whole slop from alcohol fermentation (Brit. Patent 888,654, 1931).

Electrolytic wastewater treatment processes were again in vogue in the 1960s and 1970s. These processes were used for the oxidation of (Miller and Knipe, 1965). Municipal wastewater treatment plants based on electrolysis were built in Norway and Italy around this time. These plants used seawater as electrolyte. Chlorine generated in the process oxidized organic matter and provided adequate disinfection (Miller and Knipe, 1965).

The use of electrolytic processes for domestic wastewater treatment waned during and after the energy crisis of the 1970s. This process became under strong scrutiny as being energy intensive, in spite of historical data showing contrary evidence. Most applications in the United States are presently limited to industrial waste treatment. For instance, electrolytic systems are used to remove dyes from textile industry wastes (NERAC, Inc., 1995) and oil and grease from wastewaters generated in industrial engine washing operations (Kramer et al., 1979).

This technology has gained acceptance in developing countries. The University of Campinas, Brazil, uses an electrolytic process to treat the effluent from a medical center (UNICAMP, 1987). The electrolytic process is complemented by a simple gravel filtration bed and chlorine disinfection. This treatment train results in 85% BOD and 90% turbidity removal efficiency. This plant consistently removes 70% of the N, 99.8% of the P and 99.8% of the fecal coliform bacteria entering the plant. The same concept is being used in Mexico, to treat wastewater from an academic institution near Mexico City (Morales, 1996). The findings at this institution are consistent to those reported in the Brazilian publication.

OBJECTIVES

The organic content of wastewaters is expressed as the biochemical oxygen demand, BOD_5, content of the water. The insoluble portion of the BOD_5 is typically associated with the total suspended solids, TSS, in the wastewater. Therefore removal of TSS from a wastewater results in a corresponding decrease in the BOD_5 of the treated water. The goal of this research is to assess the energy requirements of an electrolytic treatment process to reduce TSS and BOD_5 from wastewater to various treatment levels. Parameters investigated in this study include the residence time, electrochemical cell spacing and unit power (i.e., power requirements per unit of cell volume). Procedures developed in this study may then be used to minimize energy consumption in the design of electrolytic processes for other applications.

PHYSICOCHEMICAL PHENOMENA

Oxidation reactions occur at the anode in an electrolytic cell. Oxidation of elemental iron to ferrous iron is anticipated when using iron or steel anodes:

$$Fe \Rightarrow Fe^{2+} + 2e^- \quad (1)$$

Ferrous iron is relatively insoluble in water at near-neutral pH conditions. This iron form precipitates as amorphous ferrous hydroxide according to:

$$Fe^{2+} + 2(H_2O) \Rightarrow Fe(OH)_{2(s,\,am)} + 2H^+ \quad (2)$$

Oxidation of ferrous to ferric iron may proceed in the oxidant region of the electrolytic cell. Ferric iron is very insoluble at near-neutral and slightly alkaline conditions. This byproduct of the electrolytic cell precipitates according to:

$$Fe^{2+} + 3(H_2O) \Rightarrow Fe(OH)_{3(s,\,am)} + e^- + 3H^+ \quad (3)$$

Electrolysis of waters is readily obtained by application of low-DC voltage to water. High redox conditions surrounding the anodic region may induce the formation of elemental oxygen as described by:

$$2(H_2O) \Rightarrow 4H^+ + O_{2(g)} + 4e^- \quad (4)$$

Hydrogen gas is also released at surface of the cathode according to:

$$2(H_2O) + 2e^- \Rightarrow H_{2(g)} + 2(OH^-) \quad (5)$$

The pH of the water tends to vary during the electrolysis process. Predominance of Reactions 2, 3 and 4 result in a pH decrease due to the formation of hydrogen ions. A decrease in the pH is found when the cathodic Reaction 5 is predominates over the acidic anodic reactions.

Several physical phenomena occur within the electrolytic cell. The amount of iron in solution and suspension increases as a result of oxidation of the elemental iron anode. Coagulation of the suspended solids is then enhanced by the presence of soluble iron species. Flocculation of coagulated solids takes place by the mild turbulence produced by the rising oxygen and hydrogen bubbles. Some gaseous entrapment occurs also during flocculation, reducing the buoyancy of the flocs. The flocculated solids rise to the cell surface and are separated by flotation. Performance in electrolytic cells emulate the results obtained in a dissolved air flotation (DAF) unit.

EXPERIMENTAL PROCEDURES

Raw wastewater from the Las Cruces Wastewater Treatment plant was placed in the rectangular glass reactor shown in Figure 1. The dimensions of the

reactor were 48 cm x 23 cm x 29 cm. Total reactor volume was 36.5 L. Five steel plates were slid vertically into grooves made on Plexiglas sheets (the Plexiglas sheets were adhered to the reactor sides and bottom). The plates were positioned at variable intervals (1.8, 3.5, 5.5 and 7.5 cm) as shown in Figure 1. The first, third and fifth steel plates were interconnected using insulated copper wire. The second plate was connected to the fourth plate.

Direct current (DC) was applied to the interconnected plates using a 12 V DC automobile battery charger. Plates number 1, 3, and 5 were connected to the positive DC source pole. Current flow was controlled by a high-capacity rheostat connected to the negative pole of the power supply. The direct current and voltage from the circuit was monitored by an electronic multimeter connected to the regulated output from the rheostat. The second lead from the multimeter was connected to plates 2 and 4. The rheostat was adjusted to provide three different voltages in the electrolytic cells (3.0, 6.0 and 9.0 V).

Samples from all the compartments were collected at intervals of 20 minutes for a total test duration of two hours. Samples were then analyzed for BOD_5, pH and TSS as described in Standard Methods, 1985. Wastewater in the right-side compartment in Figure 1 received no electrolytic treatment. This water was also monitored for TSS and BOD_5 removal. Results from these tests were used to compare the efficiency of the electrolytic treatment schemes against conventional settling (i.e., primary treatment).

RESULTS

Table 1 summarizes the main characteristics of the raw wastewater samples used for the three voltage tests. The TSS concentration for the 6.0 V test was 175 mg/L. Other TSS concentrations were not measured in this study. Average current applied to each electrolytic cell, I, is also reported in Table 1.

Samples collected at 20 min intervals for the duration of the test (2 Hr) were analyzed for BOD_5. The fractional BOD_5 removal efficiencies, η, (with respect to theBOD_5^0 values reported in Table 1 were calculated according to the following equation:

$$\eta = \frac{BOD_5^0 - BOD_5}{BOD_5^0} \tag{6}$$

where BOD_5^0 represents the BOD_5 of the untreated wastewater samples. Table 2 presents the BOD_5 removal efficiencies for each of the experimental studies. Unit power consumption, W, for the corresponding tests is also presented in the same table. The value of W (Kw-Hr/m^3) is computed according to:

$$W = \frac{Iv}{V} \tag{7}$$

where v is the potential applied (V) and V is the cell volume (m^3).

INTERPRETATION OF RESULTS

The BOD_5 removal efficiency may fits well the following empirical model:

$$\eta = 1-(1-\eta_0)e^{-kW} \tag{8}$$

where k is a constant, and η_0 is the removal efficiency for the cell receiving no electrolytic treatment (with respect to the BOD_5^0 values in Table 1).

Equation 8 is presented as a linear expression by solving its logarithmic form as:

$$W = \frac{1}{k}\ln(1-\eta_0) - \frac{1}{k}\ln(1-\eta) = b - \frac{1}{k}\ln(1-\eta) \tag{9}$$

Thus, a plot of W against the value $\ln(1-\eta)$ generates a straight line whose slope is the inverse of -k and its intercept, $b = \ln(1-\eta_0)/k$. The computed k and η_0 values generated by using this technique are presented in Table 3. The values in this table are then used to compute the estimated BOD_5 removal efficiencies against unit power in Figures 2a, 2b and 2c for 3.0, 6.0 and 9.0 V respectively. The experimental points from Table 2 are also presented in these Figures.

Figures 2a, 2b and 2c show that the slopes of the lines decrease with applied voltage. This is also noticed by the decreasing k values with applied voltage in Table 3. Lowest slopes for any given cell are found in the 9.0 V test. In general, the k values in the 3.0 V test are slightly higher than those calculated for the 6.0 V experiment. Therefore for any selected removal efficiency, power requirements are minimized as the voltage is decreased.

The trends in Figure 2a and the corresponding coefficients in Table 3 indicate that it is theoretically possible for the 3.0 V cells to match the efficiencies observed in the 6.0 V test at somewhat lower power requirements. However, to attain such conditions the detention time in the 3.0 V tests must be nearly double those in the 6.0 V experiments. The small energy savings observed in the lower voltage cells is unattractive considering the incremental capital investment costs required by a larger reactor to accomplish similar results.

Table 2 shows that BOD_5 removal efficiencies at 9.0 V are superior to those at 6.0 V conditions during the first few minutes of the test. These trends are reversed after treatment times above 40 to 60 min. Figure 2c shows that

energy consumption in the 9.0 V tests is considerably greater than the unit power requirements measured in the lower voltage tests for similar efficiency conditions. This difference explains the low k values in Table 3 for the higher voltage test. The economic aspects associated with the lower efficiencies in the 9.0 V reactors and concomitant higher energy demand rule out the higher voltage condition as an economically feasible alternative.

It is interesting to observe the effect of cell spacing on treatment performance. Figures 2a, 2b and 2c show an increase in treatment performance with increasing cell spacing. In fact, in all cases the efficiency in the 1.8 cm cell was surprisingly low considering the high power requirements. Similar findings are shown for the 3.5 cm cell at 6.0 V conditions (experimental error led to discarding results in the 9.0 V test as shown in Table 3). The low efficiency conditions in these cells may be attributed to the formation of excessive oxidized iron.

Excess iron is known to counteract coagulation processes (Weber, 1972). The excess positive iron ions sorb onto the colloidal surfaces, thus reversing the initial negative charge colloidal matter in the aqueous suspension. Electrostatic repulsion between the particles hinders floc formation during the flocculation process. The information in Figure 3a tends to confirm that excess iron is found at high unit power conditions. This figure shows no removal of TSS in the 1.8 cm cell and a sudden drop in TSS removal in the 3.5 cm cell at 6.0 V conditions. In fact, the TSS in the 1.8 cm cell was greater after 20 min than the initial TSS concentration in the cell. Excellent solids removal is observed in both the 3.5 and 5.5 cm cells between 80 and 100 minutes treatment time. A maximum of 73% of the TSS is removed in the 3.5 cm test at after 100 min treatment time.

Electrostatic repulsion induced by charge reversal on the colloidal matter may explain the drastic efficiency reduction in the 3.5 cm cell at times greater than 100 min. This adverse phenomenon is not observed in the 5.5 cm cell. Figure 3a shows that the TSS removal in the 5.5 cm cell approaches 60% between 100 and 120 minutes treatment time. A similar trend is observed in the 7.5 cm cell, where the TSS removal increases rapidly over the first 20 minutes and then stabilizes near the maximum at 40 minutes treatment time. However, the TSS removal efficiency in this cell is never greater than about 30% for the duration of the test.

The effect of power consumption on TSS removal is visualized in Figure 2b. This figure shows that the unit power consumption in the 7.5 cm cell is nearly double that in the 5.5 cm cell for equivalent removal efficiencies. The high power requirements to remove TSS in the narrower cells limit their application in treatment practice. This finding is also compatible with the conclusion regarding the limitations of the narrow cells for BOD_5 removal.

The solution pH increased over the duration of all tests. This increase was a direct function of the applied power. Figure 3c shows the pH conditions between 0 and 120 min for the 6.0 V test. These increasing trends are attributable to the predominance of Reaction 5. Therefore formation of hydrogen gas and hydroxide from water electrolysis appear to predominate over the reactions near the anode (Reactions 1 through 4).

The pH increase may represent an effluent disposal problem. For example, Figure 3c shows that after 120 min the pH in the 6.0 V test increases to 11.8 in the 1.8 cm test. At the opposite extreme, the pH in the 7.5 cm cell approaches 8.6 in the 7.5 cm cell within identical time and voltage conditions. The pH in the 5.5 cm cell fluctuates near 9.0 after 80 minutes treatment. . Therefore, the pH increase may be mitigated by reducing input power to the cells. Therefore, power consumption is easily controlled by reducing voltage and/or increasing cell spacing as shown in Table 1.

CONCLUSIONS

Detention time, applied voltage and cell spacing affected the BOD_5 and TSS removal efficiencies in the electrolytic cells. High voltage (9.0 V) and narrow spacing (1.8 and 3.5 cm) produced low treatment efficiencies with corresponding high unit power demands. These low efficiencies are attributed to excessive oxidation of the metallic-iron electrodes. The presence of excess oxidized iron in the cells increased the TSS of the product water and it appeared to restabilized the colloidal organic matter.

Poor efficiencies were also observed in tests experiencing low applied voltage (3.0 V) within the test duration (120 min). Optimal treatment conditions occurred in the 6.0 V tests using an intermediate cell spacing (5.5 cm). These test conditions generated maximum TSS and BOD_5 removal efficiencies while minimizing power consumption. The efficiencies under these experimental conditions approached 60% for both TSS and BOD_5 removal for a 100 min treatment time. Applied unit power was 2.3 Kw-Hr/m^3 and the pH of the treated water was approximately 9.0 for these optimal treatment conditions.

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Table 1.

Initial Conditions in Electrolytic Cells

v		BOD5	I (Amp)			
Volt	pH	mg/L	1.8 cm	3.5 cm	5.5 cm	7.5 cm
3	7.24	190	0.72	0.36	0.24	0.18
6	7.68	210	1.54	0.77	0.51	0.38
9	7.82	240	2.88	1.44	0.96	0.72

Table 2.

BOD_5 Removal Efficiencies and Power Consumption in Electrolytic Cells

P	time	Control	Cell Spacing							
			1.8 cm		3.5 cm		5.5 cm		7.5 cm	
Volt	min	η	η	W KW-Hr/m3	η	W KW-Hr/m3	η	W KW-Hr/m3	η	W KW-Hr/m3
3.0	20	21	21	0.85	26	0.22	21	0.09	21	0.05
3.0	40	21	21	1.69	26	0.43	26	0.18	26	0.10
3.0	60	26	21	2.54	37	0.65	32	0.28	26	0.15
3.0	80	26	21	3.38	42	0.87	37	0.37	26	0.20
3.0	100	26	26	4.23	42	1.09	37	0.46	26	0.25
3.0	120	26	26	5.07	42	1.30	37	0.55	32	0.30
6.0	20	14	33	4.28	33	1.10	33	0.47	14	0.26
6.0	40	14	33	8.56	33	2.20	57	0.93	43	0.51
6.0	60	21	43	12.85	33	3.30	57	1.40	48	0.77
6.0	80	21	43	17.13	33	4.41	57	1.87	62	1.03
6.0	100	21	43	21.62	38	5.51	62	2.34	67	1.29
6.0	120	21	48	25.69	38	6.61	62	2.80	67	1.54
9.0	20	21	29	10.09	54	2.60	33	1.11	33	0.62
9.0	40	21	33	20.31	54	5.19	33	2.23	33	1.21
9.0	60	26	38	30.40	54	7.85	38	3.31	33	1.83
9.0	80	26	42	40.61	54	10.45	38	4.42	42	2.42
9.0	100	26	42	50.70	54	13.04	46	5.53	42	3.04
9.0	120	26	42	60.80	42	15.64	42	6.65	46	3.66

Table 3.

Computed η_o and k Constants

P		Cell Spacing			
Volt	Const.	1.8 cm	3.5 cm	5.5 cm	7.5 cm
3.0	k	0.026	0.323	0.604	0.584
	ηo	0.166	0.184	0.173	0.193
6.0	k	0.014	0.023	0.295	0.665
	ηo	0.271	0.285	0.280	0.179
9.0	k	0.004	*	0.047	0.091
	ηo	0.266	*	0.264	0.252

* Eliminated due to experimental error

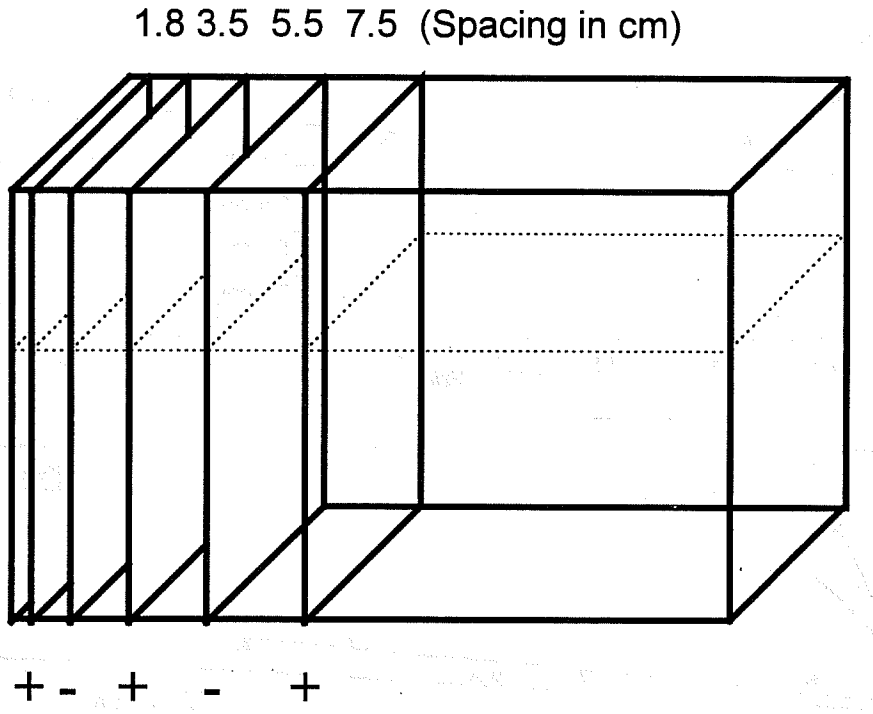


Figure 1. Electrolytic Reactor

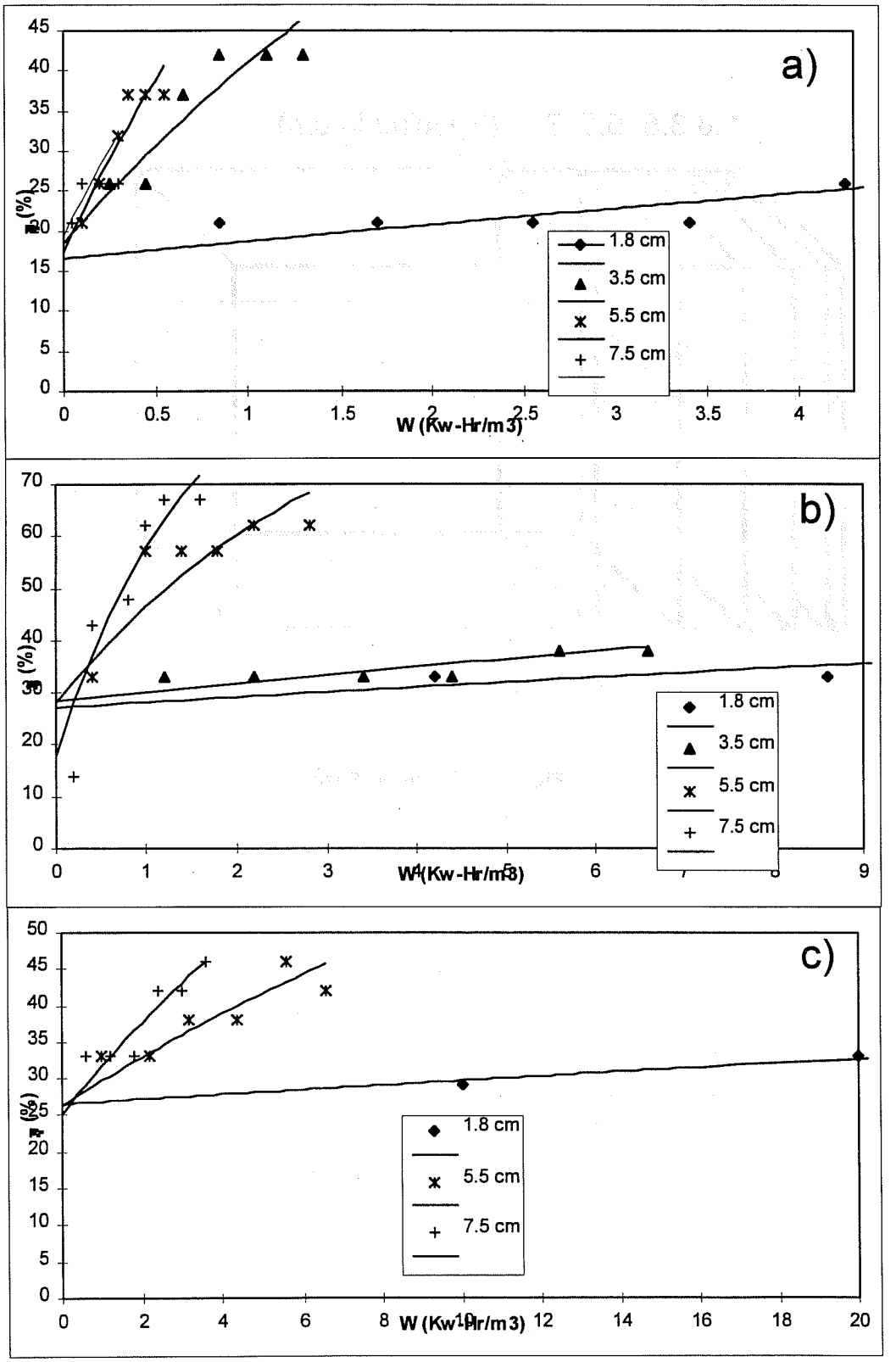


Figure 2. BOD_5 removal efficiencies at: a) 3.0 V, b) 6.0 V, c) 9.0 V

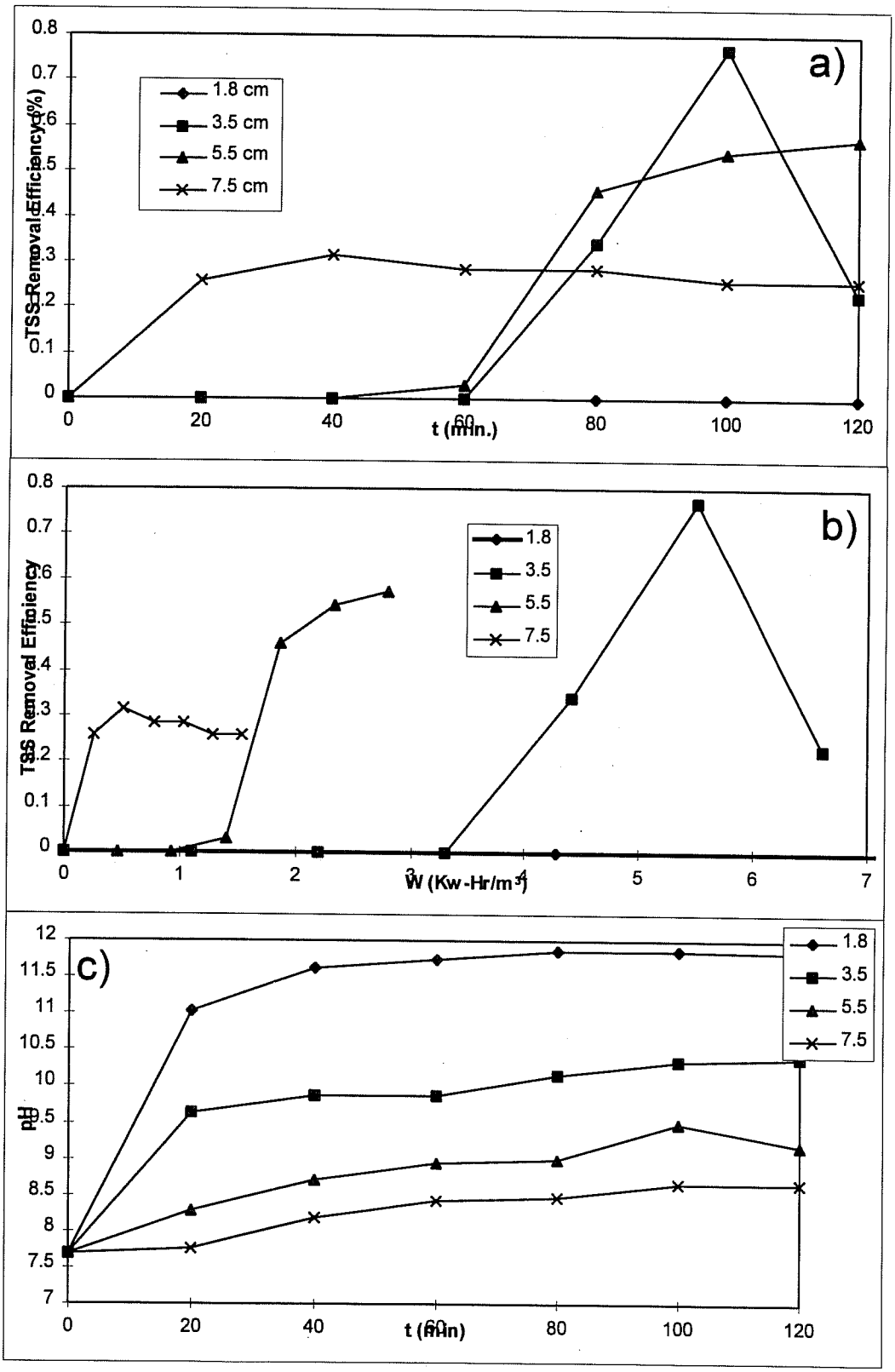
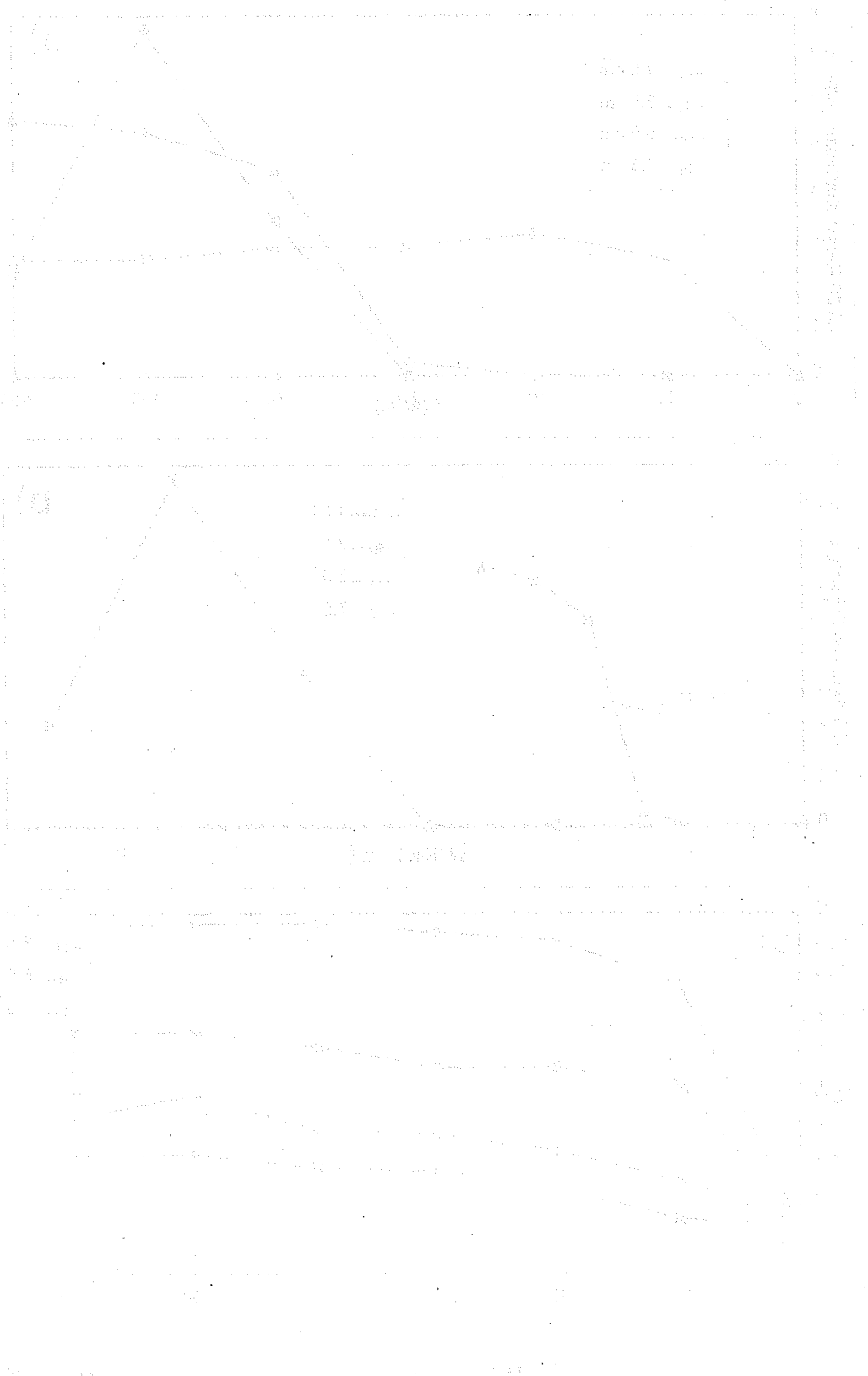


Figure 3. TSS removal in the 6.0 V test as: a) time function, b) unit power function and c) pH change with time.



Use of Injection Wells for Refinery Waste Disposal

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Abstract:

Currently regulated by the United States Environmental Protection Agency (USEPA), injection wells used for refinery related disposal are typically either Class I hazardous or non-hazardous, depending on RCRA classification. The expense of acquiring an operating permit for these types of wells is very high and they have substantially more operational expenses than a typical Class II injection well.

Class II injection wells are authorized statutorily because the injectate is associated with fluids originating from the production of hydrocarbons. The use of Class II wells at refineries has been rejected because they are not seen as being directly associated with the production of oil & gas. Examples of such refinery wastes are those associated with various treatment or process streams originating from the plant. Although these wastes are associated with produced hydrocarbons, USEPA does not consider them to be in the same category as wastes associated with Class II injection wells, even if they are characteristically similar.

The Ground Water Protection Council (GWPC) and several member companies have begun a study to address several technical and regulatory issues related to the use of injection wells at refineries. The results of this study may be utilized as justification for possible modification of USEPA classification of injection wells used for refining waste.

Purpose of Project

Statement of Problem

The U.S. Environmental Protection Agency (USEPA) currently regulates injection wells used for disposal of refinery related waste as either Class I hazardous or non-hazardous depending upon the RCRA classification of those waste. The expense of acquiring an operating permit for these types of wells is very high as are the operating expenses once a permit is obtained. Such permitting requirements as the non-migration petition, stringent construction and initial well integrity assurance requirements, intensive monitoring and reporting make these wells uneconomical even though their use as waste disposal facilities is legitimate and deemed by many as the environmentally safe option.

There are several regulatory barriers which have caused the current dilemma.

(1) The Classification System for injection wells was created back in the late 1970's when the environmental pollution concerns were source driven. In other words, the derivation of the waste, rather than its relative impact on the environment or on human health or its chemical constituency served as a basis for UIC well classification; Class I, industrial and municipal, Class II, oil field or hydrocarbon storage related; Class III, solution mining; and Class V, any other type. Only Class IV, in some sense was a more encompassing method of classification because it dealt with a situational issue; that of disposal of waste (source undefined) into or above an aquifer.

(2) The Classification System was an easy to understand, easy to implement, bureaucratic vehicle which put all injection wells into a selection of slots, much like a post office sorting system; if its a postcard it goes for 20 cents and if it's a letter of a certain weight, it goes for 29 cents or 52 cents, etc. Very little scientific data went into the creation of the Classification System.

(3) The passage of the Resource Conservation and Recovery Act (RCRA), while the first recognition that chemical constituency was an important delineation for determining hazardous exposure levels for humans and the environment, also resorted to an agonizing set of bureaucratic barriers to implement the program on a common regulatory playing field. Such standards as Toxicity Concentration Leaching Potential (TCLP) were designed to measure leaching of toxic substances from landfills but have been misapplied to other temporary or permanent surface waste holding facilities, for example, oil field drilling and reserve pits. TCLP's predecessor, EP Toxicity and the other major characteristics which define a hazardous waste, have a mixed scientific relationship when it comes to the issue of injection into a saline environment. Disposal of muriatic or hydrochloric acid with a pH of 2 or less has practically no environmental impact since the acid dissociates into hydrogen and chloride which are the same elements that make up formation brines.

(4) The most recent example of how ill-conceived reporting requirements, have little or nothing to do with protection of the environment or the health of humans is the Toxic Release Inventory (TRI). The disposal of wastes into Class I industrial waste injection wells (hazardous or non-hazardous) should not be considered a toxic release to the environment. The proposed expansion of this reporting concept to Class II oil field injection wells only expands a thought process which was ridiculous from the outset. For example, the environmental impact of 1,000,000 barrels of defined treated hazardous waste when injected into a formation 4,000 feet below surface through six wells located on a one-half mile square tract of land in a state which has 83,000 sq miles is not representative of the hazard to the State. The TRI shows this state to rank high in the release of toxic substances. All of the injection wells used to receive this waste have been permitted with the construction

standards required for Class I hazardous waste injection wells, so it is difficult to understand why such waste streams are termed toxic releases in the first place.

This project effort is intended to provide an in-depth analysis of certain refinery waste streams which have more of the chemical composition and characteristics of Class II injection well fluids. A practical regulatory approach to disposal requirements for refinery waste appears to be revision of the well classification system based on the characteristics of the identified waste streams. Initial introspection into the issue indicates that process rather than the need for enhanced environmental protection is the reason for disallowing refinery waste streams into some injection disposal situation other than Class I.

This study, in keeping with the various regulatory reinvention principles supported by the Clinton administration and the current Congressional initiatives to have risk assessment and cost benefit analysis done on environmental regulations, will provide guidance to EPA, state regulators and industry on achieving the goals of both the Administration and Congress. The last objective is to assist EPA in formulating a more realistic regulatory program for injection of refinery waste. A concept to always keep in mind is that a reduction of available refineries due to costs of waste disposal/barrel of oil processed contributes to the impedance of oil production because the cost of transportation of oil is deducted from the per barrel profit to the operator. On marginal wells, such costs are a determinant of longevity of many stripper and marginal wells.

Introduction

In 1974, Congress passed the Safe Drinking Water Act (SDWA) with the provisions in Sections 1421(a)(2) and 1422(C) that subsequently promulgated EPA Underground Injection Control (UIC) regulations not "interfere with or impede" oil and gas production unless such regulations were "essential to the protection of underground sources of drinking water or the health of humans". The concern of Congress in 1974 was two-fold:

(1) To eliminate endangerment of drinking water sources and

(2) To minimize unnecessary constraints on energy production while addressing (1) above.

Congressional discussion also stressed the desire to leave primary authority for regulating UIC wells with the states. This desire for state environmental program management for UIC somewhat conflicted with the general tenor of Congressional philosophy of the time and that was to provide strong Federal overview of state water pollution control programs through strict primary grant conditions and sets of Federal rules and regulations on such matters as surface discharge of industrial waste; reporting, containment of pollution spills, including oil and construction of municipal wastewater treatment facilities. The first piece of environmental control legislation was passed by Congress in 1972 with the enactment of the Federal Water Pollution Control Act (FWPCA). Federally driven environmental program management emanating from the early stages of implementation of FWPCA was the philosophie de jour and the U.S. Environmental Protection Agency (EPA) was mandated to handle this very complicated act and work with the states as best they could.

As with any new mandate, mistakes are made and not all on one side of the issue. In the case of the FWPCA, EPA approached their overwhelming task with enthusiasm, idealistic zealotry and only a vague understanding of many of the issued addressed by

FWPCA. States and the regulated industry erroneously adopted postures that heavy handled and prescriptive regulation was unneeded and projected considerable recalcitrance and often derision toward EPA's efforts. Because of this "cats in a bag" situation, EPA adopted the internal bias that industry was going to contest even the most reasonable approach to improving their pollution control programs and states were both turf protective and probably unknowledgeable about how to establish proper water pollution control standards and regulations. Unfortunately for both states and the regulated industries, EPA read the early 1970's mood more right than wrong. The result has been a lot of reporting, measuring, monitoring and program justification which states and industry have had to perform at considerable expense.

This extreme level of distrust by EPA still prevailed in 1976, when on August 31st of that year, they proposed the initial Underground Injection Control (UIC) regulations. Naturally, these first UIC regulations were met with significant adverse reaction, particularly from the oil and gas industry and also from the oil and gas regulatory agencies in producing states. As a result of that reaction, Congress enacted the 1977 amendments to the SDWA which included the addition of Section 1421(b)(3) requiring EPA to "consider varying geological, hydrogeological and historic conditions and existing state injection control programs in promulgating UIC regulations". The Congressional charge to the EPA administrator was that national guidelines be sufficiently flexible to take account of these varying conditions in the administration of the UIC regulatory program. The counsel from Congress to EPA once again stressed that regulations should not interfere with or impede the production of oil and gas unless "necessary" to provide non-endangerment to underground sources of drinking water.

For the first time, the term "unnecessarily disrupt" was introduced into the scenario which caused the House of Representatives to narrow the impact of the amendment and prevented unnecessary and improper legal challenges to the Administrators regulations. The interpretation of "unnecessarily disrupt" finally boiled down to the prohibited structuring of the Federal, or national programs which were so inconsistent

with specific requirements that neither the national and state requirements could be successfully implemented. An important interpretation was that if both state and national requirements can be met even at a substantially higher cost, the national requirements could not be deemed disruptive.

In 1980, Congress passed P.L 96-502, known as the Waxman Amendment which added Section 1425 to the SDWA. Section 1425 allowed oil and gas states to obtain primacy for Class II oil and gas injection well programs based on a states "demonstration" that their program was already effective and met the four statutory requirements of Section 1421(b)(1). Approved state UIC programs must:

(1) Prohibit underground injection not authorized by permit or rule;
(2) Provide that no permit will be issued, or rule promulgated, which "endangers drinking water sources";
(3) Include inspection, monitoring, record keeping and reporting requirements; and
(4) Apply to federal agencies or injection on federal lands.

Impact of 1980 Amendments

Section 1425 formed a precedent which was the recognition by Congress that unnecessary strictures placed on the oil and gas producing industry and the state agencies regulating the industry could:

(1) Disrupt and potentially negate the efforts of many state oil and gas, or in some cases, environmental regulatory agencies efforts to protect water and environmental resources from substandard UIC practices. Many states had viable UIC programs in place years before the advent of SDWA in 1974 and the potential diversion of industry and state regulatory personnel from field activities to overview activities such as

monitoring and reporting was a realistic concern. Reallocation of personnel to oversight activities could be paralleled to the old adage of the alligators and the drainage of the swamp.

(2) Unreasonably disrupt or impede the production of oil and gas without proving that elevated levels of regulation and program oversight were necessary to protect the environment and human health.

The passage of Section 1425 was also an acknowledgment that the original well classification system set up by EPA for all classes of wells under Section 1422 was, in many cases, overly burdensome with administrative requirements and that Class II injection well programs could suffer under the onus of regulation which Section 1422 potentially suggested. The important questions which should have been asked in 1976 or in 1980 was whether the Class I through V Injection well categories provided the desired level of flexibility in UIC waste management. Under Section 1425, a demonstration of equivalent effectiveness could be made. Under Section 1422, states and EPA in those states not choosing to take program primary, were under stricter dictates of the Federal Rules and Regulations and the opportunity for demonstrating equivalent effectiveness was not available. States, as a part of primacy assumption and approval by EPA had to develop regulatory programs for classes of wells which were not represented in the state; for example, setting up a Class II regulatory program for a state with no oil or gas production.

Proposed Work Plan and Timetable

Phase I: Characterize the Various Wastes Produced at Refineries: Work effort will include:

(1) Accumulate available data from the refining industry that have been done toward characterization of waste. Characterization will be analyzed on the basis of:

(a) Chemical composition of individual waste streams or aggregate waste streams, whichever is applicable.

(b) Delineation of waste stream chemical constituency in terms of hazardous versus non-hazardous characterization under current regulatory framework.

(2) Obtain any studies or refinery waste characterization data amassed by the US EPA.

(3) Compare data received under (1) and (2) above.

(4) Obtain information on hydrogeologic, geologic and injection zone availability in the vicinity of refineries. Information to be obtained from refineries, state geological surveys or regulatory agencies.

(5) Make visitations to at least ten refineries in Texas, Louisiana, Utah and California. Selection of visitation sites may be driven by any regional variations in waste characteristics formed under (1) or (2) above.

Time Table -- Phase I activities (1)-(5) will take place between April 1, 1996-June 30, 1996 and will be simultaneous and coordinated with several refineries or groups of refineries depending upon logistics.

Phase II

Phase II will be centered around a comparison of the refinery waste streams data collected under Phase I with the common waste characteristics of oil field produced water waste streams being injected into Class II wells. Work efforts under this phase include:

(1) Visitation to any refineries in states which appear to have different geologic or hydrogeologic situations but were not included under Phase I; Illinois, Washington Pennsylvania, or New Jersey. The reason for visits to states with no oil production such as New Jersey or Washington is to determine:

(a) The potential for subsurface injection of refinery waste in states where waste injection is non-traditional and perhaps prohibited.

(b) The current attitude of state agencies in nonproducing states on refinery waste injection or the practice of industrial waste period.

(2) Correlate data on waste characteristics of waste streams authorized for injection into Class II wells. These are wastes which EPA has termed exempt from Hazardous Waste (Subpart C) regulations and the exemption has allowed identified streams into Class II wells. This activity may start prior to the anticipated end of Phase I.

(3) This phase will also include a preparation of both cost/benefit analysis in terms of the degree of environmental protection gain for a variety of disposal mechanisms. A similar analysis will be made of the potential risk from these disposal options versus the cost/environmental benefit from a selection of EPA UIC well class, i.e. Class I, Class II or a separate class for selected refinery wastes. This activity will continue into Phase III because it has to do with the feasibility of various injection well scenarios.

Time Table -- Phase II activities (1) and (2) will take place and completed during the period July 1, 1996-September 1, 1996. Any Phase II information garnered as a part of Phase I will allow acceleration of the project. Part (3) background will occur during Phase II but the bulk of feasibility analysis will occur in Phase III.

Phase III -- This phase will be concerned with the following activities:

(1) Completion of the part of the study having to do with risk assessment, cost/environmental benefit analysis and discussion of the disposal options relative to each.

(2) A discussion and set of recommendations as to how the various refinery waste streams fit into the EPA UIC Well Classification System.

(3) Discussion of any changes to the Well Classification system which appear desirable to put refinery waste into a more cost effective/environmentally beneficial mode.

(4) A critique of how the injection of refinery wastes can, depending upon the regulations, impede or assist in stabilizing the production of oil and gas. This is in keeping with the original intent of the SDWA in 1974 and 1977.

Time Table -- Completion of Work Elements to be Accomplished by October 15, 1996.

Sonochemical Treatment Of Refinery Wastewater

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Abstract

Studies of the destruction of BTEX compounds in water were undertaken using a Near Field Acoustic Processor (NAP). It is demonstrated that this magnetostrictive transducer based system is capable of degrading Benzene and Toluene in a CSTR configuration. Pseudo first order rate constants were dependent on both the applied power and the target compound concentration, indicating higher order reaction kinetics. The pseudo first order rate constant ranged from 0.003 min^{-1} to 0.03 min^{-1}. The energy efficiency of the conversion in this system is shown to be lower than other advanced oxidation processes, and suggestions are made regarding possible methods to improve this technology.

Introduction

The treatment of wastewater prior to discharge to prevent deterioration of water quality continues be a significant environmental engineering challenge. This continued need has challenged engineers and scientists to explore new methods for pollution control. Ultrasonic irradiation is one of the newer methods whose potential as a water and waste water treatment technique has not been explored extensively. The two most common types of transducers used for generating ultrasound in aqueous solutions are piezoelectric and magnetostrictive. Magnetostrictive transducers are inherently more rugged, and therefore ideally suited for industrial use (1). Despite this, only a single paper in the literature reports the use of this transducer for treatment of waste water (2). In this paper we demonstrate that the NAP magnetostrictive reactor is capable of degrading benzene and toluene in a flow through configuration.

Ultrasound refers to sound waves with frequencies higher than those to which the human ear can respond (>16 kHz). The upper limit of ultrasonic frequency is not sharply defined but is usually taken to be 5 MHz for gases and 500 MHz for liquids and solids. Power ultrasound enhances chemical reactivity through cavitation. Acoustic cavitation generally refers to cases involving both expansion and contraction of cavities or bubble nuclei and which ultimately leads to implosion of the bubble (3). Suslick *et al.*, (4) have

determined that the gaseous contents of a collapsing cavity may reach temperatures of 5500°C, and that the liquid immediately surrounding the cavity approaches 2100 °C. The pressure was estimated to be 500 atmospheres. These temperatures and pressures are of course very short lived and localized, but the chemical effects of cavitation have been thoroughly documented (4). In addition, it has been shown through electron spin resonance studies that, during cavitation, water molecules are broken into free radicals that provide another mechanism for contaminant oxidation (5,6). The focus of this paper is the use of power acoustic cavitation to effect the destruction of benzene and toluene contaminated aqueous waste streams.

APPLICATION OF SONICATION TO WASTE TREATMENT

The effect of sonication on the degradation of a wide variety of compounds in aqueous systems has been demonstrated using piezoelectric horn systems. Hoffmann *et al.*, (7) investigated the kinetics & mechanisms of the sonochemical reactions of p-nitrophenol in oxygenated aqueous solutions. They concluded that in the presence of ultrasound (20 kHz, 84 W), p-nitrophenol was degraded primarily by denitrification and that the reaction products & the kinetic observations are consistent with a model involving high-temperature reactions of p-nitrophenol in the interfacial region of cavitation bubbles.

Jiann *et al.*, (8) demonstrated that ultrasonic process is a promising and effective method for the destruction of low concentrations of chlorinated organic compounds such as CCl_4 in water. Removal efficiencies of greater than 99% were achieved through this process. The sonochemical degradation at 530 kHz of pentachlorophenate in aqueous solutions saturated with different gases resulted in fast cleavage of the carbon-chlorine bond releasing Cl^-, mineralization of PCP to CO2 when the solution is saturated with oxygen, CO production if argon is the saturating gas, nitrite and nitrate formation when the reaction is conducted with aerated solutions (5). Cheung and Bhatnagar (9) irradiated chlorinated C1 and C2 volatile organic compounds in dilute aqueous solution with 20 kHz ultrasonic waves in a sonochemical reactor (0.1kW/L) under ambient temperature and pressure conditions. They found that the percentage destruction varied from 72 to 99.9%.

It is evident that ultrasonic irradiation has the potential to be an effective method for the destruction of organic contaminants in water because of localized high concentrations of oxidizing species such as hydroxyl radical and hydrogen peroxide in solution, high localized temperatures and pressures and the formation of transient supercritical water (7,10,11). However, with only one exception (2) all these studies have been carried out using the piezoelectric probe type of reactor. The probe type of reactor is not the optimum reactor configuration for the efficient generation of transient cavitation for two reasons. The sonication efficiency is reduced because of the "blanketing effect" caused by the intense generation of bubbles (12). Hua *et al.*, (2) have shown that the G value (a concept of efficiency commonly used in radiation chemistry - the number of molecules formed or destroyed for each 100 eV deposited in the substance) for the probe reactor is approximately an order of magnitude less than in the NAP although the rate constants are of the same magnitude. In addition, the probe type transducers have a relatively short life, while magnetostrictive transducers are more robust and better suited for industrial application. In this paper, we explore the effects of operational parameters

(flow rate, applied power, substrate concentration) on the efficiency of a NAP and compare these results with other oxidation processes from the literature.

Materials and Methods

Chemicals: Reagent grade benzene and toluene were used as received for this study (Fisher Scientific).

Reactor system: The NEARFIELD Acoustical Processor (NAP, Lewis Corporation, Oxford, CT), is a dual frequency ultrasonic reactor with thermal control. The NAP's reaction vessel consists of opposing diaphragm plates operating at 16 kHz & 20 kHz. The use of dual frequencies eliminates standing waves. The diaphragm plates form two of the walls of the reaction vessel. The ultrasonic cavitation field intensity can be adjusted by varying the power fed by the generator, up to 500W per plate is available in either filtered or unfiltered mode. The use of different spacers allows the NAP reactor to be configured to investigate the effect the power/volume ratio on the kinetic parameters for the treatment aqueous solution. A 22 L glass carboy was used as the stock solution reservoir. All connections were made with stainless steel fittings and tubing. presents a schematic of the reactor. An HPLC pump (Waters, Inc.) was used to feed the reactor. The flow rate was adjusted between 3 and 10 mL min^{-1}. Two reactor configurations were used, one with only the Gore-tex^{tm} gasket separating the transducer plates and a second with a 1/8th inch thick stainless steel spacer included. The reactor volumes were 163 and 310 mL respectively.

EXPERIMENTAL PROCEDURE

Preparation of stock solutions: Benzene or toluene was spiked directly into the 22 liter glass reservoir using a mechanical micropipette. Stock concentrations of either 4 mg/L, 40 mg/L, and 80 mg/L were used.

Experimental runs: Experiments were performed using stock solutions saturated with air and oxygen. Preliminary testing using a recirculating mode of operation demonstrated that pre-saturating the solution with oxygen was sufficient to maintain the oxygen level near saturation for the course of 60 minutes sonication. Thus to prevent volatilization of the analyte from the reservoir during the sonication, the reservoir was pre-saturated with oxygen prior to starting the pump. The pre-saturation consisted of sparging the reservoir with pure oxygen for 20 minutes. In the case of air saturation, no action was taken to treat the water; equilibrium with the air is assumed. The effluent concentration from the reactor was monitored until a stable value was reached, and a pseudo-first order rate constant was computed from the observed decrease in effluent concentration.

ANALYTICAL METHODS

A liquid chromatography method was developed to determine the solute concentration in water using a Bio Rad HPLC system with a variable wavelength UV detector (204 nm). A C-18 reversed phase column was used for the analysis (Enviro-sep-PP, Phenomenex, Inc. Torrance, CA). The separation was effected by isocratic elution

using a 60:40 mixture of acetonitrile : water at a flow rate of 0.7 mL min^{-1}; direct injection of 20 μL of the reactor effluent onto the HPLC system was possible with this configuration. External calibration with gravimetric standards was used.

RATE CONSTANTS

The pseudo first order rate constant for each run was calculated from the following relationship which is based on the assumption that the sonic irradiation resulted in the reaction chamber being well mixed.

$$C_{in} = \frac{C_{eff}}{1 + k\tau} \quad (1)$$

where C_{eff} is the effluent concentration (mM); C_{in} is the stock solution concentration(mM); k is the pseudo first order rate constant (min^{-1}), τ = V/F is the residence time (min); V is the reactor volume and F is the volumetric flowrate (mL min^{-1}). Average values of C_{in} and C_{eff} were used in the computation of k.

Reactor efficiency: The energy transfer efficiency of this reactor must be determined in order to determine its potential for industrial applications. The NAP was characterized by the calorimetricly to determine the efficiency of energy transfer to the water. The system was operated in batch mode, and was filled with 302 g of water. The system temperature was monitored for 45 minutes during sonic irradiation. After stopping the sonication, the temperature decrease was followed as the reactor cooled to room temperature. The post-sonication temperature drop was used to estimate an overall heat transfer coefficient from the reactor system to the surroundings. The heat lost to the surroundings during sonication was assumed to be governed by this overall heat transfer coefficient. A heat balance provides a measure of the energy input to the water which was compared to the power taken from the wall.

Results and Discussion

A series of experimental conditions were investigated with the aim of determining the effectiveness of sonolytic destruction of benzene and toluene. The effects of the operational parameters reactor volume, flowrate, and applied power were considered.

Figure 2 presents typical results from the operation of the NAP as a continuous stirred tank reactor (CSTR). For the data presented, the reactor volume was 310 mL and the flow rate was 5mL min^{-1} providing a residence time of 62 min. Sonication at 100W/plate results in approximately 15% conversion of benzene, while at 300W/plate the conversion is 55%. The return of the effluent concentration to the inlet concentration after stopping the sonication demonstrates that the observed reduction in benzene concentration is the result of the treatment and not due to sorption or volatilization from the reservoir.

Effect of contaminant concentration: The sonolytic reaction is not intrinsically a first order reaction because the production of free radicals mediated by the cavitation in the system is a function of the applied power. Thus at high contaminant concentrations,

the observed rate should be zero order in the contaminant. The observed pseudo first order rate constant as a function of contaminant concentration is presented in Figure 3. Note that at the high concentration the pseudo first order rate constant becomes approximately independent of the contaminant species, as would be expected for a second (or partial) order reaction limited by the species concentration (approximately constant) which is incorporated in the pseudo first order rate constant. Analytical precision prevented experimental work at higher concentrations.

Effect of applied power: The pseudo first order rate constant dependence on the applied power density is shown in Figure 4. The power density is the total applied power divided by the reactor volume. Power density was found to be a better correlation variable for the pseudo first order rate constant in this system than the power intensity (based on the transducer surface area in contact with the solution being treated). Two points for the toluene data do not correlate well with power density, however, the data were collected near the end of a 12 hour period in which oxygen sparging in the reservoir was not used. Previous studies in which the dissolved oxygen (DO) content was monitored with time in a recirculating system which indicated that the O_2 concentration was stable over a period of 2-3 hours, but it is not known for the runs in question whether the O_2 concentration remained at a high enough level to provide a moderate cavitation threshold. It has been observed that for low DO sonolytic efficiency decreases (13). The implication of this correlation is that in order to maintain relatively high power densities, the reactor design should incorporate multiple transducers which are closely spaced. One possibility for achieving this would be to design porous plate transducers for the wastewater to flow through. Data in the literature indicates that at sufficiently high power intensities, the coupling between the transducer and the wastewater is affected by the intense cavitation near the transducer surface and the sonolytic efficiency begins to drop (2); for the range of power densities used in this study, this effect was not observed.

Reactor efficiency: The efficiency of the NAP with regard to substrate conversion is dependent on several factors which include the efficiency of the conversion of electrical to sonic energy in the transducer, transmission of the transducer vibrations to the water, the fraction of the acoustic power used for inception of cavitation, the intensity of the cavitation event, and the production of free radicals associated with the cavitation. This NAP was characterized in terms of transfer of electrical energy (from the wall outlet) to the water by assessing the temperature rise of the water as described above. As can be seen in Table 1 the overall calorimetric efficiency is less than 10%, thus there is considerable room for improved energy conversion efficiency in this system.

Table 2 presents a comparison of the chemical conversion efficiencies of several advanced oxidation processes. It is apparent from this comparison that in the configuration used in this work, that ultrasonic treatment of wastewater is at the low end of the range of efficiencies when compared to other options currently being studied. However, the system has not been not optimized for energy efficiency, and we are currently exploring methods to increase the cavitation efficiency. Some of the options under consideration include combining ultrasound with other advanced oxidation processes such as hydrogen peroxide treatment, ozonation or UV photolysis. We are also investigating the possibility of using electrolysis in the reactor chamber to provide

oxygen bubble nucleation sites. The hypothesized benefit of this is that the cavitation threshold will be reduced (14) and therefore the sonic energy which had been consumed in surface creation will be available for cavitation, and free radical production.

CONCLUSIONS AND RECOMMENDATIONS

This work has demonstrated the sonolytic destruction of benzene and toluene in a Near Field Acoustic Reactor. First order pseudo first order rate constant were computed from the data, and were found to be in the same range as previously reported for piezoelectric horn systems. The pseudo first order rate constant was observed to be a function of the substrate concentration as would be expected in a situation where the number of free radicals available for the oxidation of the substrate is determined by the power input. The pseudo first order rate constant for benzene varied from $0.014min^{-1}$ to $0.004min^{-1}$ as the reactor feed concentration varied from 4 mg/L to 80 mg/L (51μM to 1030μM), while the pseudo first order rate constant for toluene ranged from $0.025min^{-1}$ to $0.004min^{-1}$ as the reactor feed concentration varied from 4 to 80 mg/L (43.5μM to 870μM).

The observed pseudo first order rate constant was found to increase approximately linearly with the power input to the system (measured as power taken from the wall). Considering all of the experimental data presented, the pseudo first order rate constant varied over approximately an order of magnitude from 0.003 to 0.03 min^{-1} for an applied power range of 0.6 to 3.6 watt/mL.

The overall efficiency of the conversion of the substrates was found to be at the low end of the range for advanced oxidation processes. We are currently pursuing a research program to investigate methods for increasing both the destruction efficiency and energy efficiency of this technology with the aim of providing another industrial scale alternative treatment. Some possibilities include: coupled hydrogen peroxide, ozone, or UV photocatalysis; and solution chemistry modification to enhance the efficiency of free radical generation through cavitation.

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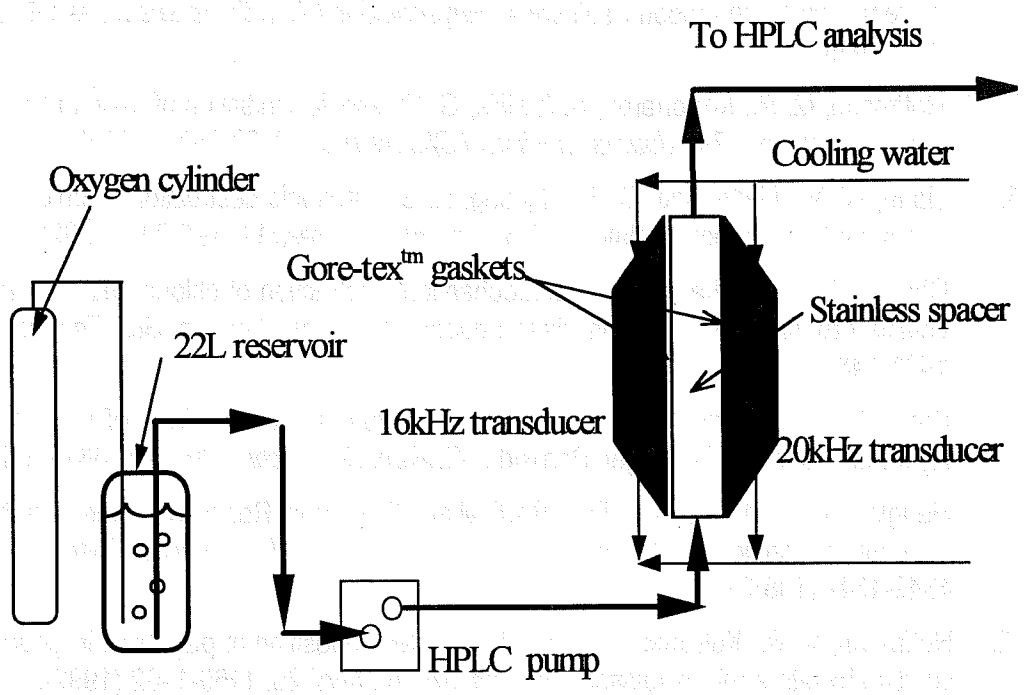

Figure 1. Schematic of experimental apparatus

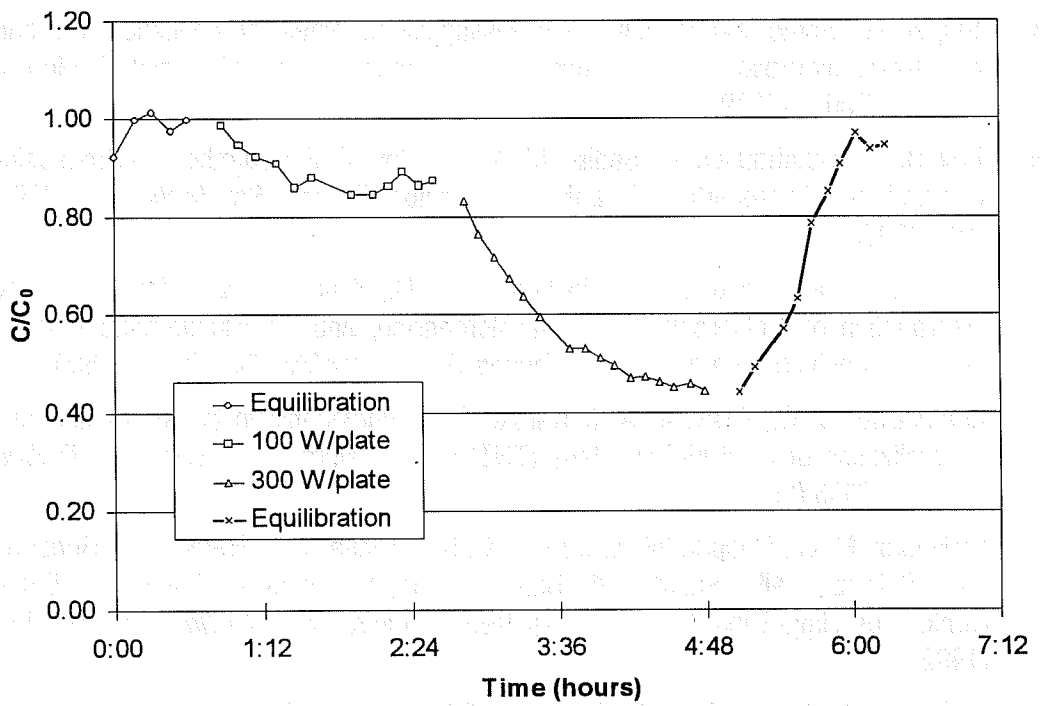

Figure 2. Transient response of NAP CSTR to changes in applied power.

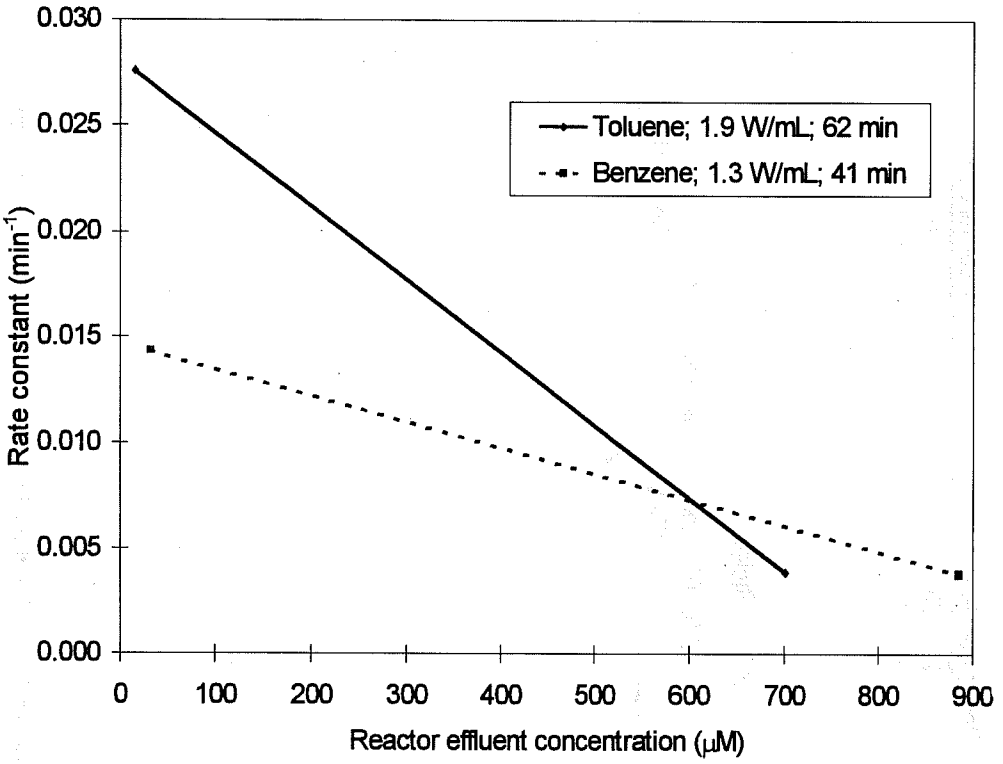

Figure 3. Sonication rate constant as function of concentration ($w/0_2$). Reactor volume 310 mL; Residence time shown in legend.

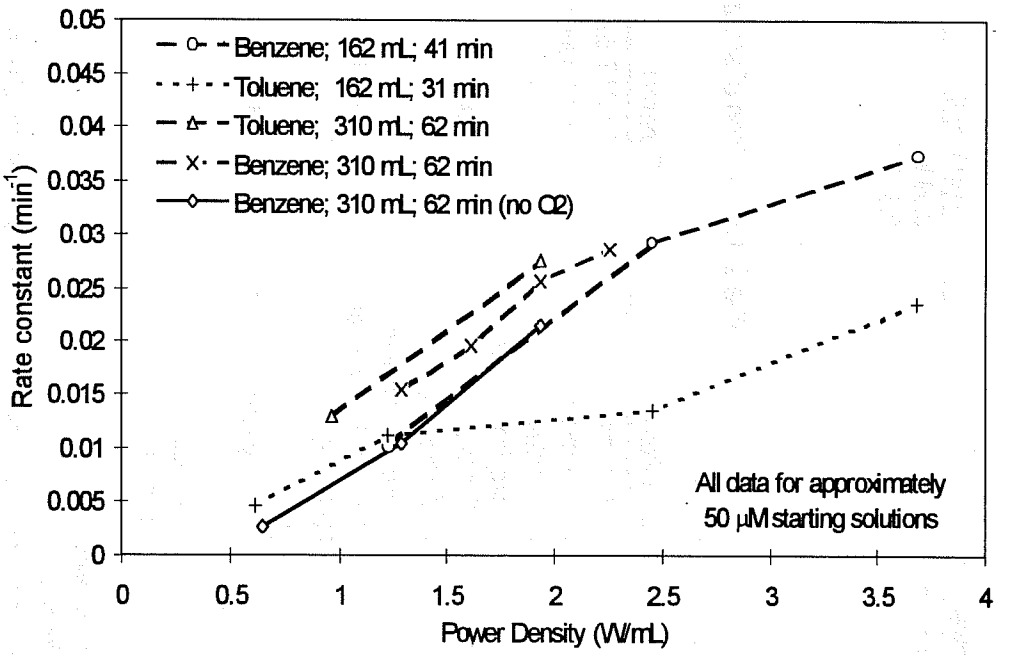

Figure 4. Pseudo first order rate constant dependence on power density; residence time in minutes.

Table 1. Calorimetric determination of energy conversion efficiency

Total power input	UA_w (average)	Power transferred	% conversion
200 watts	0.39 W/°C	19.25 watts	9.6
800 watts	0.65 W/°C	57.8 watts	7.1

Table 2. Comparison of advanced oxidation process efficiency

Process	Conditions	Chemical	G (x 10^4), molecules destroyed per 100eV supplied	Conversion
US NAP (this work)	1.9 W / mL	1000μM Toluene	2.2	19%
	τ = 62 min	50 μM Toluene	0.37	63%
US NAP (2)	7.27 W/mL recirculating batch	100μM p-nitrophenol	6.9	
US Probe	4.8 W/mL	100μM p-nitrophenol	0.37	
Hydro-thermal (15)	450°C; 650 bar; τ =60 sec; titanium	1,1,1-TCE	0.16	99.96%
EHD[b] (16)	120 x 7kJ discharges	4-chlorophenol	28	35%
UV/TiO_2 (17)	250 watt 45 min	TNT	0.14	99%
Electron Beam (18)	7.94 J/g absorbed dose[c]	17μM benzene	190	93%
UV/TiO_2 (19)	100 watt 4 hours	TNT	9	99%

[a] Supercritical water oxidation
[b] Electrohydraulic discharge
[c] The large G value for this work is partially due to the basis for the calculation being the absorbed dose rather than the power required to apply that dose.

Use of Commercial Cultures in

Preventing Amine Upsets in a Texas Refinery

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InterBio
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Abstract

Amines, frequently used in removing sulfur compounds from sour crudes, often carryover into many petrochemical facilities wastewater treatment streams. The amines stress the system at three points: (1) inorganic oxygen demand, (2) organic oxygen demand, (3) ammonia loading. This study reviews a recent experience at a major Texas refinery. This facility incurs problems with maintaining nitrification with the release of a di-glycol amine (DGA) stream that is used in processing sour crude. Entry of DGA into the activated sludge system increases pressure on heterotrophic organisms and inhibits autotrophs (nitrifiers) farther into the system. As a result, the refinery uses diversion tanks to store water with high levels of DGA with a goal of bleeding the off specification water into the system. Due to the high cost of storage, the refinery studied the effect of exogenous cultures on preventing system upset. Using cultures provided by InterBio/Microbe Masters, the refinery used proactive dosing to effectively process water with high levels of DGA.

Introduction

Over the course of several years, the refinery has found a strong correlation between di-glycol amine (DGA) releases and wastewater treatment system upset. Since DGA is highly soluble in water, it could not effectively be eliminated from the waste stream entering the activated sludge plant by existing primary treatment. Amines, including DGA, are strong emulsifying agents used in removing sulfide from crude streams in petroleum refining operations. These amine compounds have a unique ability in destabilizing water treatment systems by impacting both heterotrophic and autotrophic bacterial populations present in activated sludge biomass. DGA can affect both since it contains an organic portion degraded by heterotrophs and a separate ammonium ion that increases pressure on autotrophic nitrifiers (Ford 1992).

Since DGA is used in stripping sulfur from crude streams in refining, sulfide bound in the sour gas may be lost to sewers in carryover, skimming situations. In this case, the waste stream entering the water treatment system contains both the original amine compound along with sulfide ions. The reduced sulfide adds to inorganic oxygen demand. This combination of inorganic sulfide, organic glycol, and ammonia has a tendency to interfere with nitrification and organic removal across the entire system (Verschueren 1983).

A rapid decrease in system nitrification forms the primary indication of an increase in amine stripper water carryover. The loss of nitrification is usually attributed to higher than normal organic and inorganic oxygen demand at the front of the system. The heterotrophic organisms already present in the biomass respond by increasing their activity level. While the heterotrophic organisms do not directly harm the nitrifier populations, the increased activity will slow nitrifier activity by reducing available oxygen and phosphate residuals. Furthermore, nitrifiers are extremely sensitive to low levels of toxics. Following many strong organic releases, autotrophs normally present begin to lose out in competition for nutrients and oxygen in the organic rich waters. In this case, the DGA molecule also releases amine units into the water. The amines are converted under anaerobic or aerobic conditions into NH_3 increasing the ammonia loading. This production of ammonia within the activated sludge basin places many refineries into problems with ammonia permit compliance (Metcalf & Eddy 1991).

In this case, the refinery had other concerns besides effluent compliance issues. With the increased ammonia loadings, the refinery had to increase chlorine usage to effectively treat the water. When wastewater has increased ammonia levels, disinfection by chlorination becomes more difficult. To effectively disinfect the same quantity of water, the facility must increase the amount of chlorine used. Increased costs in direct chlorine use and associated operator time proved

significant to the refinery's operating budget. In addition, the refinery also had to use diversion water techniques to maintain permit compliance with the release of DGA. This involved the use of storing water in tankage normally reserved for use by processing. The refinery requested an evaluation of their system by Microbe Masters to determine potential methods of reducing the impact of DGA upon the system (Metcalf & Eddy 1991) (Manahan 1991).

System Evaluation for DGA Impacts

To assist the refinery, Microbe Masters began a program of data collection on all sources of DGA entering the water treatment system. After consulting refinery personnel, three (3) sources of DGA contaminated water were located. The refinery's environmental personnel began testing the streams to find more precise correlations between DGA levels and activated sludge system upsets.

All DGA emissions from Sour Water Stripper Tanks 1, 2 and 3 were closely recorded. In addition, the refinery personnel worked with Microbe Masters in creating a dosing program using commercial cultures in the aeration basin.

The dosing program instituted by Microbe Masters included plans for reducing the need for diversion water to handle DGA, lowering the amount of chlorine needed for effluent disinfection, and keeping the system within ammonia permit levels with DGA entering the ASB (activated sludge basin).

Chlorine use falls with decreased ammonia loadings at the tertiary treatment section. In the presence of ammonia, disinfection requires the use of substantially more chlorine. Therefore, a reduction in ammonia levels also decreases use of chlorine in the final treatment section. (Rodina 1972)

After reviewing the data collected, Microbe Masters determined that system failure occurred when DGA increased F/M ratios, increased inorganic oxygen demand, and increased ammonia loadings at the front end of the system. To counteract this effect, Microbe Masters chose to use Micro Pro D, a dry product containing strains of heterotrophic bacteria that were isolated and stress acclimated from multiple petrochemical waste streams. The addition of Micro Pro D works by increasing the amount of effective acclimated biomass in response to increased "food" from a DGA release. Based on DGA present in Tank 1 the following dosing was instituted:

DGA Loading from Tank 1	Dosing Response
0 - 10 mg/L	10 lbs Micro Pro D
11 - 25 mg/L	15 lbs Micro Pro D
26 - 100 mg/L	25 lbs Micro Pro D
101 - up mg/L	50 lbs Micro Pro D

The basic goal of the instituted program was to increase the number of active heterotrophic bacteria at the head of the system to a point where the glycol from the DGA molecule would be easily consumed in the first stages of treatment. By having the ability to quickly increase biomass, the refinery could degrade the DGA waste without the lag normally seen when not using Micro Pro D. The lag effect resulted in nitrification at lower than desired levels. Therefore, Microbe Masters designed the dosing schedule to maintain all hydrocarbon degradation within the historical heterotrophic area of the basin. Increased ammonia levels incurred with DGA releases would be handled within the existing nitrification zone. If the DGA were to increase ammonia levels over the current handling ability, Microbe Masters had a secondary option of adding additional nitrification cultures to the basin.

Figure 1 presents DGA water from Tank 1 and the associated ammonia levels in the effluent. From the graph, Microbe Masters found a strong relationship between DGA leaving Tank 1 and rapid increases in effluent ammonia numbers. Before the use of microbial additions, an increase of 15 mg/L DGA frequently pushed ammonia levels at or above permit levels. Traditionally, DGA flows ran at approximately 7.85 mg/L into the aeration basin.

In testing the impact of adding Micro Pro D, the refinery increased DGA entering the system to 84.4 mg/L with no statistically significant effect upon effluent ammonia. This provides strong evidence of Micro Pro D's impact upon system kinetics. The increased number of active acclimated bacteria at the front end of the system brings about a rapid lowering of carbonaceous BOD_5. The quick reduction in BOD_5 loadings allows for nitrification to occur in the final section unimpeded by heterotrophic organism activity and toxics from non-degraded organics.

Figure 2 gives the relative COD levels in the Tank 1 effluent. With the program instituted DGA levels increased by a factor of ten (10) on average; a corresponding increase in COD levels is also noted in the graph. With both DGA and COD loadings increased, Microbe Masters then examined the new data generated at the effluent.

Figure 3 gives the effluent COD plotted against DGA entering the system from Tank 1. Historical COD levels have been within the 140 range, but with the increase in influent COD over an extended period, Microbe Masters anticipated some adjustment. With the first increase of DGA entering the system in late November, COD levels peaked. As the additions of Micro Pro D continued, the COD levels began decreasing to more normal levels. In a second major release of

DGA in late December, the COD level increased with the DGA concentration, but the system quickly adjusted. Microbe Masters expects COD levels to remain in the 190 mg/L range when DGA releases are maintained at approximately 80 mg/L.

The greatest effect of adding cultures is best presented by Figure 1. Prior to adding Micro Pro D as DGA was released, ammonia levels at the effluent exceeded permit levels with half of all minor releases. Since such excursions were unacceptable, the refinery began holding water contaminated with DGA until a better disposal method could be located. However, with the improved DGA capacity, the refinery released DGA in much greater quantities than before. The result was only one reading of ammonia at permit max over a 30 day period of releasing DGA at levels that would have broken permit only a few weeks before.

Conclusion

With the refinery facing disposal problems and increased treatment costs, Microbe Masters found an opportunity to use a proactive dosing program to handle a problem waste stream. By using existing facilities to deal with DGA, the refinery saved on diversion water costs, chlorine usage, and potential problems with loss of nitrification. The alternatives for the refinery were clearly not attractive since all involved extensive capital expenditures, or reoccurring high cost off-site disposal. After instituting the proactive dosing of Micro Pro D, the refinery found that the existing wastewater system could handle increased quantities of DGA in the wastewater treatment system.

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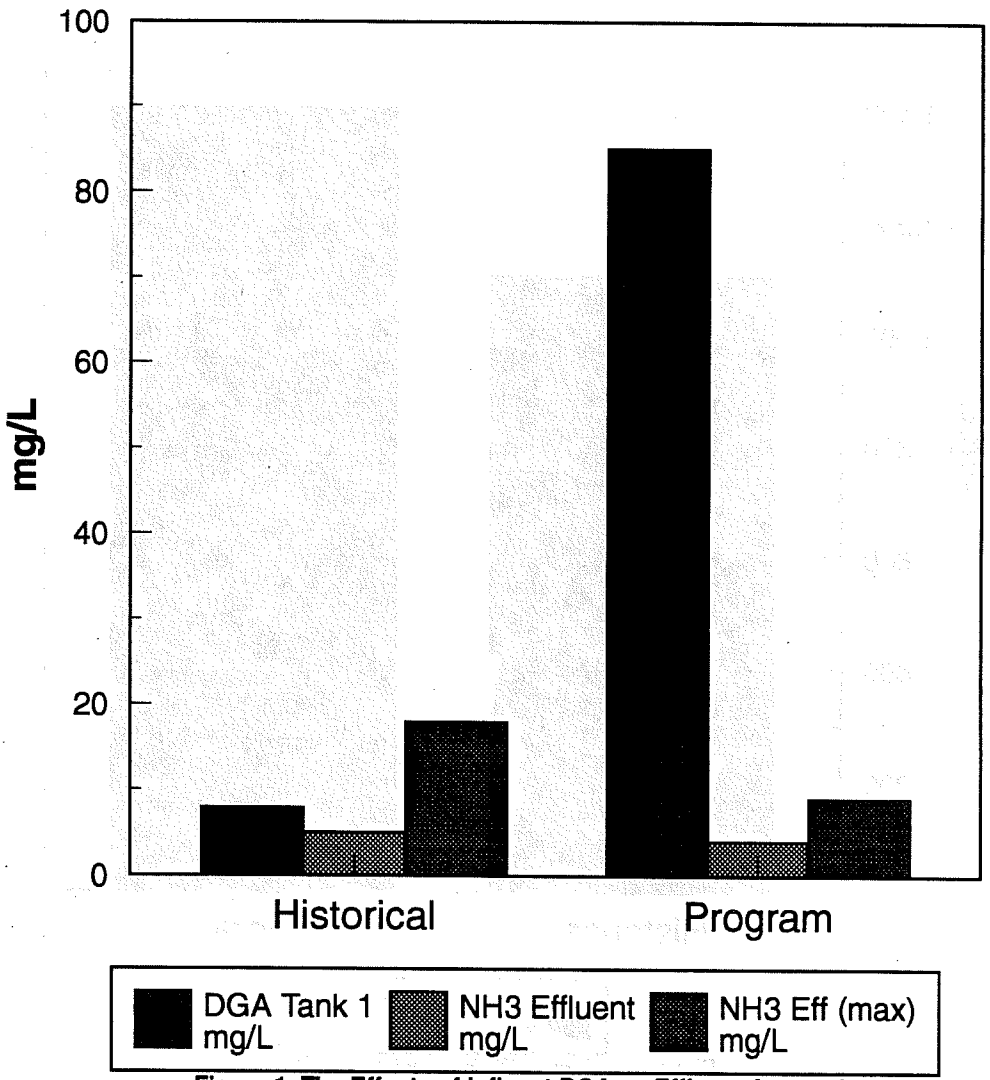


Figure 1. The Effects of Influent DGA on Effluent Ammonia

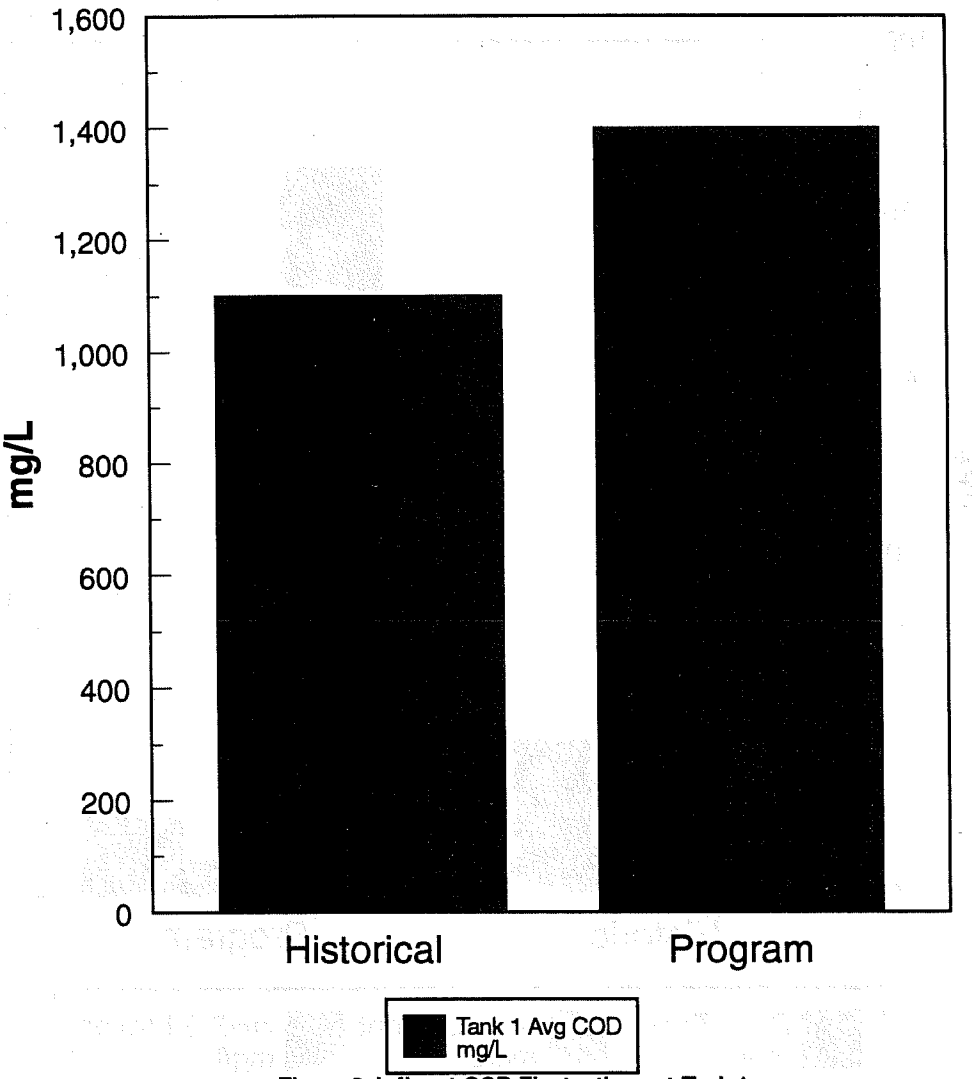


Figure 2. Influent COD Fluctuations at Tank 1

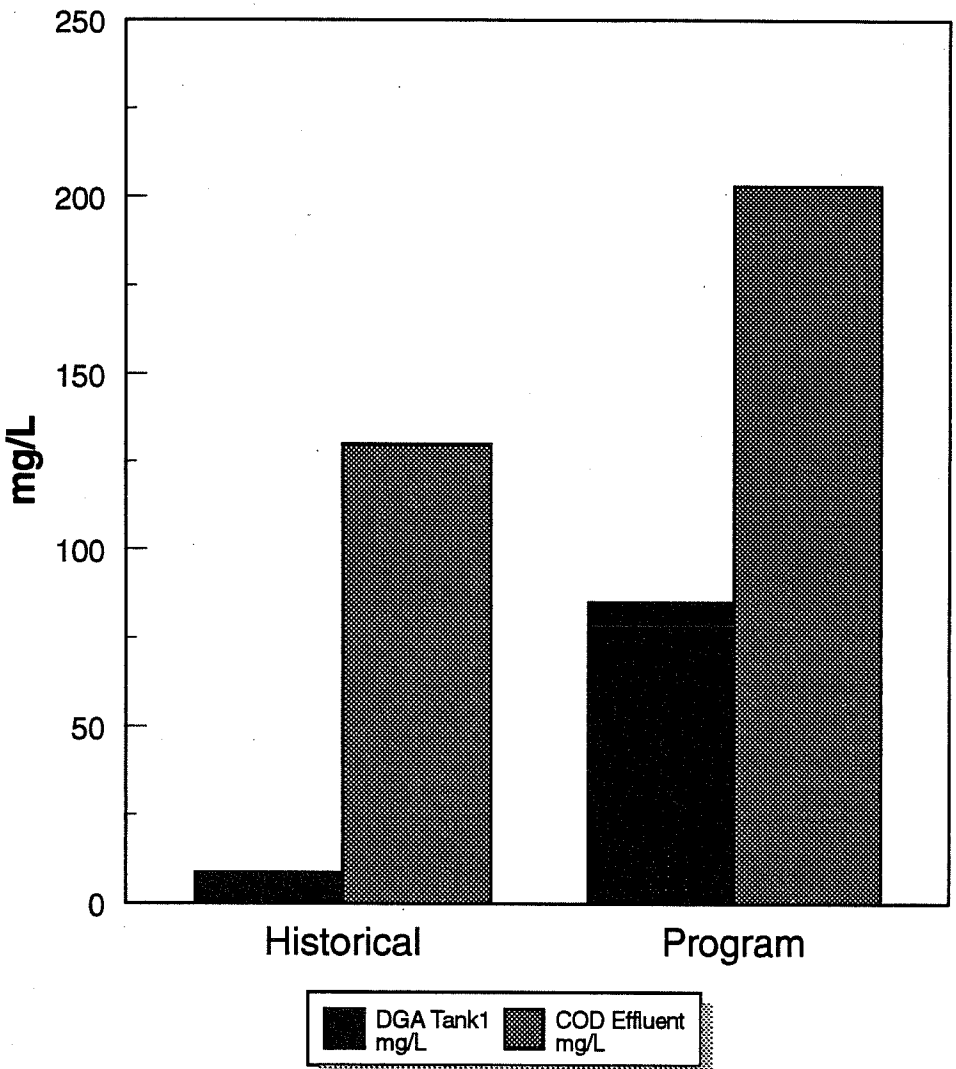
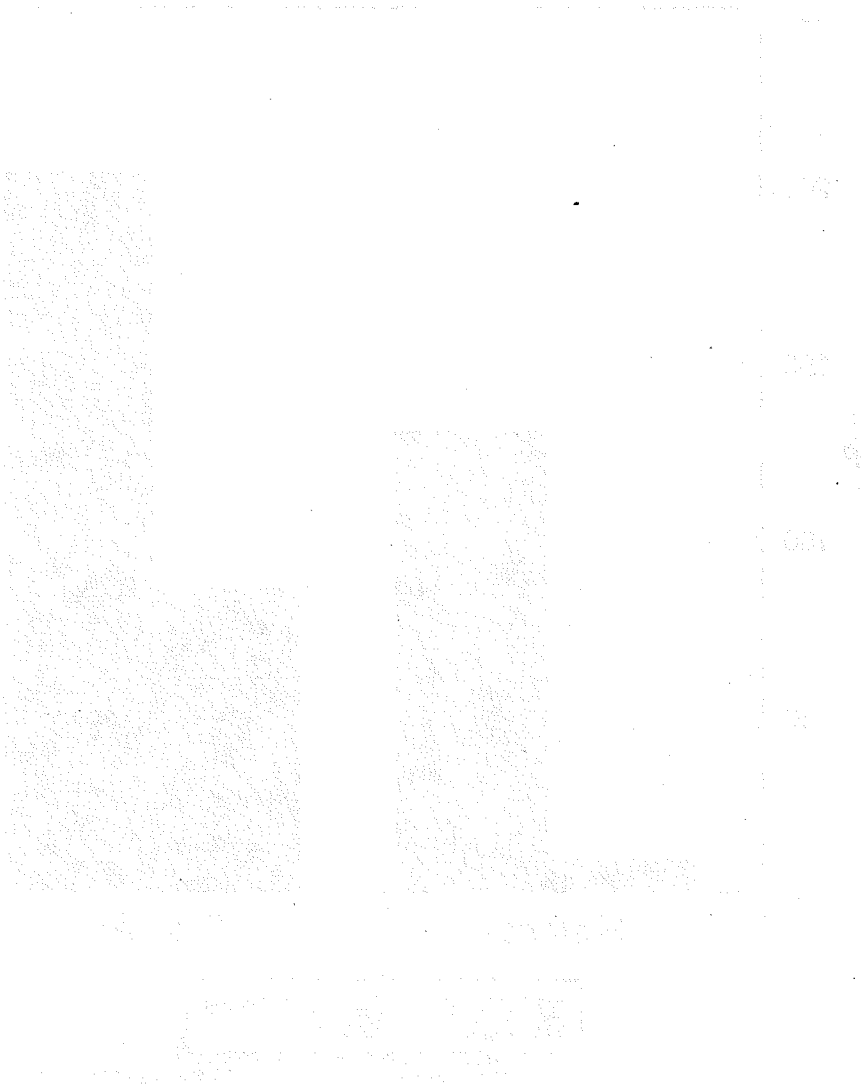


Figure 3. DGA Concentration in Tank 1 and Effluent COD



Macro Porous Polymer Extraction for Hydrocarbon/Water Separation

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MPP Systems

Akzo Nobel's Macro Porous Polymer Extraction (MPPE) technology effectively removes dissolved hydrocarbons in ground- and process water by combining liquid-liquid extraction and steam stripping with an innovative medium. Excellent performance in removal of BTEX and other petroleum hydrocarbons coupled with simple, robust design make MPPE an attractive process for petroleum and natural gas environmental applications.

Hydrocarbon contaminated water is passed through a column packed with MPPE particles. An extraction fluid, immobilized within the polymer matrix, draws the hydrocarbons out of the water. All hydrocarbons with an affinity for the extraction fluid (compared to water) are removed. The extraction fluid does not leach into the treated water. Regeneration is accomplished in-situ with low-pressure steam. The steam volatilizes the hydrocarbons but not the immobilized extraction fluid. Volatilized hydrocarbons are condensed then separated from condensate by gravity. The hydrocarbon product is available for recycle or re-use.

MPPE systems achieve removal efficiencies of 99.99% for wide varieties and combinations of aliphatic, aromatic, and chlorinated compounds. MPPE has shown consistent performance over a broad range of flow rates and concentrations. Operating units include saturation-level BTEX removal from natural gas dehydration process water, and aromatic extraction from a mixed-contaminant groundwater stream.

MPP Systems, a new business activity of Akzo Nobel, offers turn-key, custom-designed MPPE units with specific performance and cost guaranteed.

INTRODUCTION

Akzo Nobel (Arnhem, the Netherlands) has developed a new polymer-based technology for the removal of both dispersed and dissolved hydrocarbons from water. The applied Macro Porous Polymer (MPP) structures are developed by Akzo Nobel and are tailor-made to deal with various water treatment problems. In this paper the application of MPPE (MPP containing an extraction liquid) for the removal of volatile dissolved hydrocarbons from water is presented.

SYSTEM CONCEPT

Macro porous polymer particles containing an extraction liquid (MPPE) are applied in a packed bed to remove dissolved hydrocarbons from ground- and process water. The MPPE particles are periodically regenerated.

During regeneration the volatile hydrocarbons are removed from the particles by steam stripping, while the immobilized non-volatile extraction liquid is retained in the pores of the polymer. After condensation of the vapor phase, an organic and an aqueous phase are obtained. The aqueous condensate is returned to the feed of the extraction column. The organic phase is separated for re-use or disposal. The regeneration time is shorter than the extraction time. As a result, several packed MPPE beds can be in the extraction mode while one MPPE bed is being regenerated with low-pressure steam. At a given required water treatment capacity, the number of MPPE columns is fully determined by economy. A schematic representation of a two-column system is shown in Fig. 1.

APPLICATIONS OF MPPE SYSTEMS

All hydrocarbons with a relatively high affinity (i.e., partition coefficient) for the immobilized extraction liquid (compared to water) are removed from water by the MPPE system.

Examples of such hydrophobic components are: aliphatic hydrocarbons, aromatic hydrocarbons (e.g., benzene, toluene) and chlorinated hydrocarbons (e.g., carbon tetrachloride, chloroform, dichloromethane, trichloromethane). Polychlorobiphenyls (PCB's) and polyaromatic hydrocarbons (PAH's) can also be extracted by MPPE.

However, the volatilities of PCB's and PAH's are too low for regeneration by steam stripping. For non-volatile hydrocarbons an MPPE system based on a different regeneration concept has been developed.

In this system the non-volatile hydrocarbons are removed from water with MPPE particles containing a relatively volatile extraction liquid. The packed MPPE bed is regenerated through contact with fresh extraction liquid. The extraction liquid used for washing the MPPE particles is recovered by distillation (see Fig. 2). The applications of the MPPE system are compared with those of alternative purification systems in Table 1.

PERFORMANCE

The applications of the MPPE systems have been demonstrated on pilot and industrial scales for both process- and ground water. For all relevant components, effluent concentrations down to 1 ppb (detection limit) or lower have been realized. The main technical characteristics of the field tests are presented in Table 2.

Effluent concentrations at ppb level are not always required. If allowed, higher effluent concentrations are applied to minimize purification costs (see Table 4 for examples).

In the first phase of every field test, extraction breakthrough curves (effluent and influent concentrations versus time) and regeneration curves (condensate concentrations versus time) are generated to determine the required operating conditions. Once the required operating conditions are known, the MPPE demonstration unit is operated fully automatically for at least one week. Influent and effluent concentrations are measured for each cycle. A typical example of a field test is presented in Table 3.

Commercial MPPE systems have been running for more than one year with the first fill of MPPE material. The main characteristics of four full scale MPPE units in operation are presented in Table 4.

ECONOMICS

For a broad range of mass loadings and effluent requirements, especially rigorous ones, the MPPE system offers lower investment and operating cost than carbon adsorption and steam stripping. An example of a cost comparison for Western European conditions is presented in Table 5.

The cost comparison is based on quotations. It is questionable whether low ppb levels are at all possible with air stripping at the indicated costs. The costs of the turnkey MPPE units include:

Investment

- Complete installation (equipment, piping, process control provisions, tracing and insulation, PLC, software)
- Operation and maintenance manual
- Engineering
- Procurement
- Construction
- Commissioning and start-up

Operational costs

- Steam
- Electricity
- Performance guarantee and service contract (including periodical replacement of MPPE material)

Optional

- Remote control
- Steam generation for remote operation
- Future: on-line analysis (ppb level; being developed)

REFINERY OPERATIONS

A distinguishing feature of the MPPE process is energy-efficient wastewater treatment with product recovery. This is particularly noteworthy in refinery operations where valuable product may be lost to wastewater at many process steps. Aromatic and aliphatic hydrocarbons may become dissolved in water streams and thereby lost to production at numerous process locations including:

- Desalters
- Cracking units
- Refining units
- Product tanks
- Slop oil tanks

MPPE is well-suited for recovery of the product as well as treatment of the water. Thus, the necessary cost of wastewater treatment is substantially off-set by marginal revenue from recovered product. The MPPE system is adaptable to individual process units as well as to collected streams of multiple process units because of its energy efficiency and modular design. Fig. 3 illustrates the MPPE process in refinery operations.

ADVANTAGES OF MPPE SYSTEMS

The advantages of the MPPE system are:

- Achievement of low effluent concentrations (ppb level) due to the large number of mass transfer stages in series and in-situ separation of extraction liquid and purified water
- Low cost, in-situ MPPE regeneration
- Reliable, robust process combining proven technologies (extraction and steam stripping) with an innovative extraction medium
- Easy operation, fully automated, limited control by operators
- Recovery of hydrocarbons for re-use or recycle, thereby mitigating off-site disposal liability
- Consistent performance over a broad range of flow rates and component concentrations
- No negative interference with possible additional treatment steps
- Low steam consumption compared with conventional steam stripping
- No scaling; extraction at ambient temperature, removal of iron and other potential precipitating metals prior to water treatment with MPPE not necessary (ground water)

The sum of these advantages is a system for water-hydrocarbon separation which is cost competitive, reliable and highly effective.

Table 1

Application of MPPE and Alternative Systems.

Component	Characteristics	MPPE	Air Stripping & Carbon	Steam Stripping	Biotreatment
Aliphatic Hydrocarbons	NV	+	-	-	+
Aliphatic Hydrocarbons	V	+	+	+	+
Aromatic Hydrocarbons	V	+	+	+	+/-
Chlorinated Hydrocarbons	V	+	+	+	+/-
PCB's	NV	+	-	-	-
PAH's	NV	+	-	-	-
Alcohols*, Ketones*	V	-	+	+	+

*Too hydrophylic for removal by MPPE

Table 2

Pilot Scale Field Tests.

Type of Water	Components	Flow Rate (m^3/h)	Influent Concentration (ppm)	Effluent Concentration (ppm)
GW	BTEX	0.2	375	< 0.001
	VCH		140	< 0.1
GW	BTEX	0.2	19	< 0.001
	VCH		0.3	< 0.001
	MO		1.6	< 0.001
GW	VCH	0.1	3	< 0.001
PW	VCH	0.5	0.1	< 0.001
PW	HCH	0.1 - 0.5	0.1	< 0.0001
	VCH		2600	< 0.001
PW	CS_2	0.3 - 0.7	50	< dl
GW	VCH	0.6	70	< 0.3
GW	VCH	0.3	30	0.02

Abbreviations:

BTEX	=	Benzene, toluene, ethylbenzene, xylene
CS_2	=	Carbon disulfide
dl	=	Detection limit
GW	=	Ground water
HCH	=	Hexachlorinated hydrocarbons
MO	=	Mineral oil
NV	=	Non-volatile
PAH	=	Polyaromatic hydrocarbons
PCB	=	Polychlorobiphenyls
PW	=	Process water
V	=	Volatile
VCH	=	Volatile chlorinated hydrocarbons
+	=	Possible
-	=	Not possible
+/-	=	Doubtful

Table 3

Typical Example of a Field Test.

Flow rate	0.5 m^3/h
Cycle time	4.0 h
Steam consumption	3.5 kg/h

Effluent concentration below 1 ppb

Hydrocarbon	Influent concentration (ppb)
Dichloromethane	900
1,2-cis-dichloroethene	460000
Trichloromethane	690000
Tetrachloromethane	810000
Trichloroethene	16100
Tetrachloroethene	620000
1,1,1-trichloroethane	3000
Hexachloroethane	62
Hexachlorobutadiene	36
Hexachlorobenzene	2

Table 4

Full Scale MPPE Units.

Main Characteristics	Unit 1	Unit 2	Unit 3	Unit 4
Type of water	GW	PW	GW	GW
Components	BTEX, VCH	BTEX	VCH, VIS	BTEX
Flow rate (m^3/h)	10	4	7	0.8
Influent concentration (ppm)	515	2000	20	76
Effluent concentration (ppm)	< 1	< 0.1	< 0.01	< 0.005
Number of packed beds	2	2	2	1
Type of operation	A	M	A	AR
Packed height (m)	4.8	2.4	2.0	1.5
Bed diameter (m)	1.6	0.8	0.8	0.5
Amount of MPPE per column (kg)	3000	375	500	150
Steam consumption (kg/h)	200	20	43	10

Abbreviations:

A	=	Automatic
BTEX	=	Benzene, toluene, ethylbenzene, xylene
GW	=	Ground water
M	=	Manual
PW	=	Process water
R	=	Remote
VCH	=	Volatile chlorinated hydrocarbons
VIS	=	Volatile inorganic solvent

Table 5

Economic Comparison of Technologies.

I. System Description

Flow rate	10 m^3/h
Influent concentration (BTEX/VCH)	515 ppm
Effluent concentration	< 1 ppm

Cost	MPPE	Steam Stripping
Investment Index	1.00	1.29
Operational index	0.19	0.27
Operational (unit removed)	1.00/kg	1.42/kg

II. System Description

Flow rate	18 m^3/h
Influent concentration (VCH)	10 ppm
Effluent concentration	< 20 ppb

Cost	MPPE	Air Stripping/Carbon
Investment Index	1.00	1.10
Operational index	0.34	0.41
Operational (unit removed)	1.00/kg	1.22/kg

Abbreviations:

BTEX = Benzene, toluene, ethylbenzene, xylene
VCH = Volatile Chlorinated Hydrocarbons

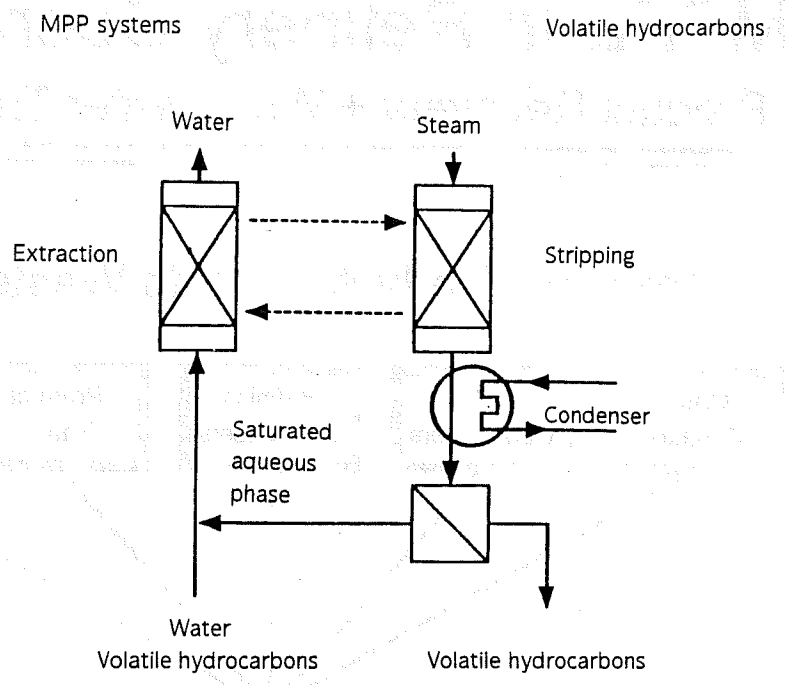

Figure 1. MPPE extraction/stripping system

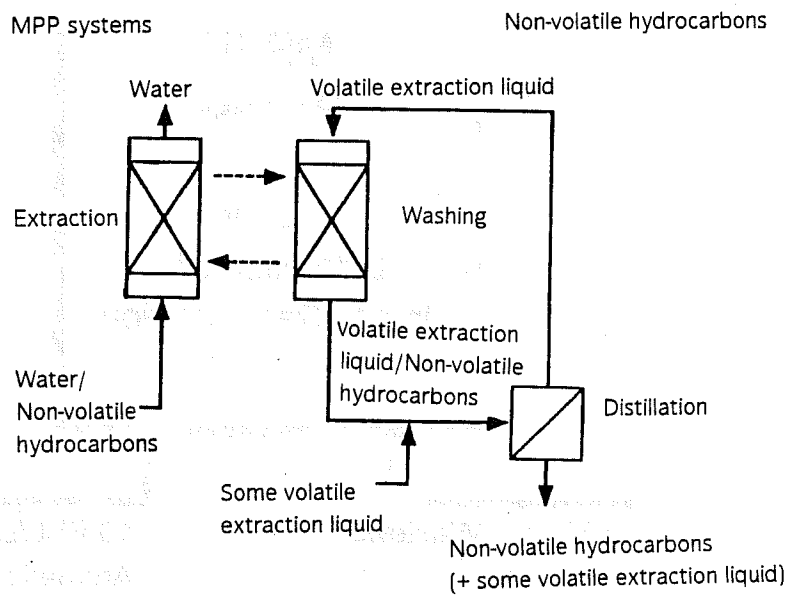

Figure 2. MPPE extraction/washing system

MPPE In Refinery Operations

Product Recovery + Wastewater Treatment

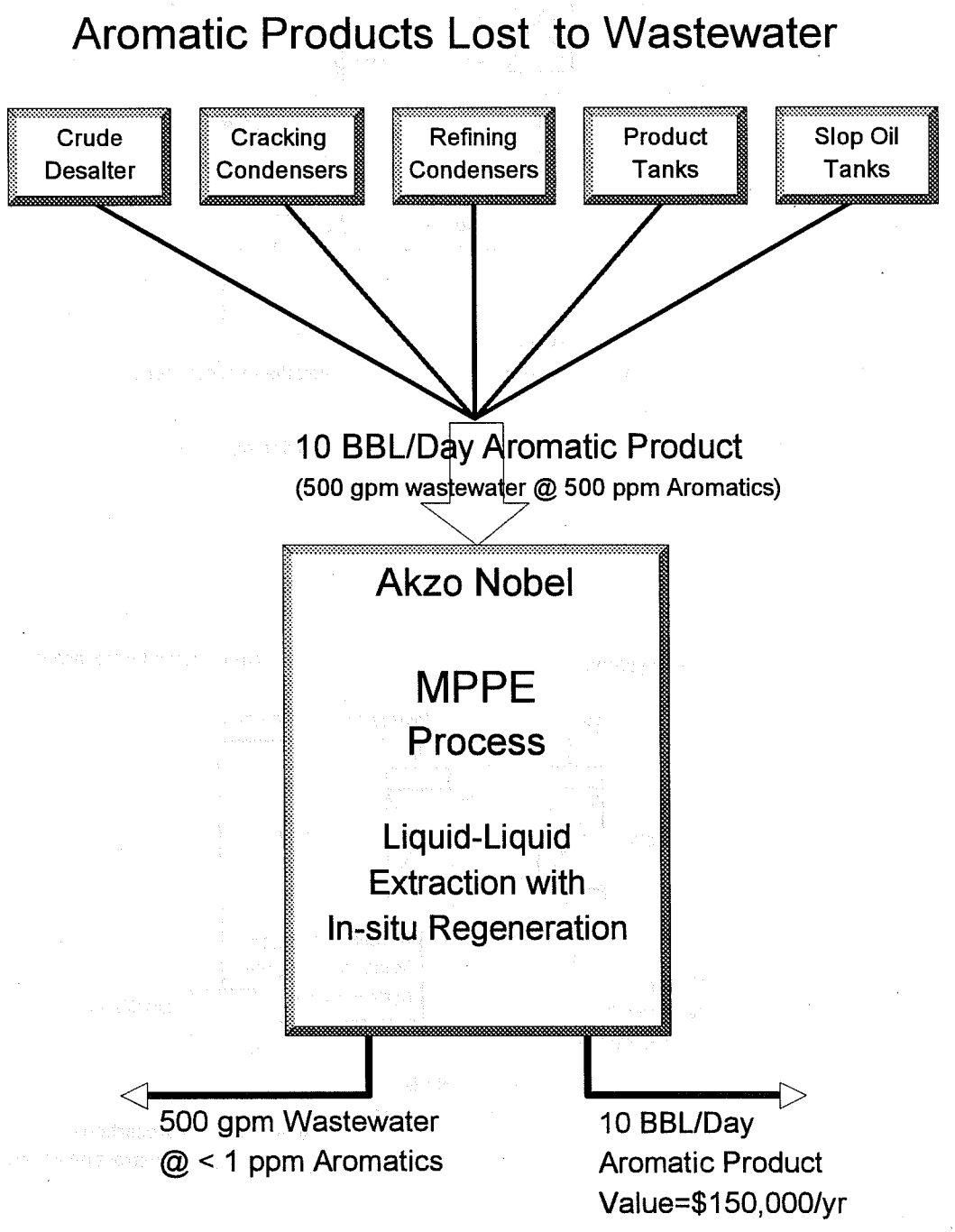

Figure 3. MPPE In Refinery Operations

Perspectives on NORM Waste Issues and Solutions

A Comparison of Radium 226 Concentrations in Oilfield Wastes Using Gamma Spectroscopy vs. Single Channel Sodium Iodide Scintillators and Portable Exposure Rate Instruments

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Abstract

Some misconceptions exist within the oil and gas industries as to the determination of Radium-226 concentrations in oilfield wastes and soil. Comparisons shall be drawn between the definative method of analysis, standard laboratory gamma spectroscopy, and a Sodium Iodide scintillator coupled to a Single Channel Analyzer (SCA). It shall also be shown that exposure rates taken on containers of waste cannot be used for the determination of Radium-226 concentrations in oilfield wastes and soil.

INTRODUCTION

With the recent and ever growing regulation of Naturally Occurring Radioactive Material (NORM), oil and gas producers and service companies are faced with a myriad of requirements to protect their personnel and the environment. One of these requirements is the proper determination of the concentration of radioactive material in their wastes, soil, lands, etc. This determination is necessary in order to meet certain regulatory requirements for transportation, release for unrestricted use, and to select the best and most proper disposal method. Standard laboratory analysis utilizing Gamma Spectroscopy is considered by most Federal and State regulatory agencies as the definitive methodology for concentration determination. However, when large sample volumes are required such as in a land remediation project, this method can become cost prohibitive. Because of this, screening methods have been developed to allow field personnel to obtain approximate results of radionuclide concentrations. Using the screening methods, field personnel can determine when release limits are being approached so that samples can be sent to a radiological laboratory for more precise analysis. This can significantly reduce overall project cost. Unfortunately, a misconception exists as to how these screening results may be used. Many companies are using these screening results as the definitive measurement for the determination of radionuclide concentrations. As a result, reported concentrations using the screening methods can be as much as 30% lower than the actual concentration determined in a laboratory environment. This results in the release of wastes and lands that are outside regulatory parameters, the possible exposure of individuals to radioactivity and radiation levels above those allowed for the general public, and the disposal of regulated materials in an unauthorized manner. This subjects the licensee to possible enforcement action from regulatory agencies, the imposition of monetary fines, and a significant increase in liability. This study will compare the results obtained through actual laboratory analysis to those obtained using screening methods actually in use in the field.

ANALYSIS METHODS

Laboratory Analysis- Gamma Spectroscopy

Laboratory analysis was conducted using a High Purity Germanium (HPGe) detector. The detector was coupled to an EG&G Ortec 92X 16,000 channel Multichannel Analyzer (MCA). The detector has a nominal efficiency of 50.4% and is equipped with a 0.5 mm beryllium endcap. A vast majority of radionuclides emit gamma radiation. Gamma radiation is always emitted at discrete energy levels. The energy of these gamma rays is measured in units of

kiloelectron volts (KeV) or megaelectron volts (MeV). The KeV is basically a measure of the intensity of the gamma ray. In gamma spectroscopy, the energy of the liberated gamma ray is measured and stored in computer memory until the sample is finished counting. Since gamma rays are emitted with discrete energies, they can be used as a "fingerprint" and can be used to identify which radionuclide gave off a particular gamma ray at a particular energy. Once the sample has finished counting, the measured gamma ray energies are compared to a master library of gamma energies and the particular radionuclide that emitted that gamma ray is identified. The amount of a particular radionuclide present is calculated and reported in a unit called the picocurie (pCi). The pCi content is then divided by the mass of the sample to give a final result in pCi/gram (a concentration). ^{226}Ra emits a gamma ray at an energy of 186.10 KeV with an abundancy of approximately 4%. ^{228}Ra is a pure beta emitter and therefore does not emit gamma radiation. ^{228}Ra concentration is determined using the principle of secular equilibrium. Secular equilibrium develops when the radioactive half-life of the parent nuclide ($T_{1/2\ P}$) is much greater than the radioactive half-life of the daughter nuclide ($T_{1/2\ D}$). Once secular equilibrium occurs, the concentration of the daughter will equal the concentration of the parent as a result of a build-up of the daughter nuclide. This will occur after approximately seven daughter half - lives ($7T_{1/2\ D}$). The immediate daughter of ^{228}Ra is ^{228}Ac (Actinium) and equilibrium will develop in approximately 43 hours. ^{228}Ac emits a gamma ray at 911.21 KeV and has an abundancy of approximately 27%. The emission of this gamma ray allows the ^{228}Ra concentration to be determined via the secular equilibrium assumption. Gamma spectroscopy measures and quantifies all gamma emitting radionuclides in a sample. This is important since most regulations pertaining to NORM do not only regulate the concentration of ^{226}Ra and ^{228}Ra, but also the concentrations of their respective progeny.

The gamma spectroscopy equipment used in this study was calibrated to a mixed gamma standard source traceable to the National Institute of Standards and Technology (NIST). All results were reported to an uncertainty level of 2 standard deviations as recommended by the EPA and NCRP Report 58. Minimum Detectable Activity (MDA) levels were calculated using methods established by Currie (1).

SCREENING METHODS

Single Channel Analyzer (SCA)

One of the most widely used methods for screening wastes and soil for NORM employs the use of a Single Channel Analyzer (SCA). SCA's can be used to discriminate against certain gamma ray energies. They can be calibrated to detect only those gamma rays that fall within an established energy "window". Gamma rays with energies that fall above or below this window will not be detected. For this study, the most common SCA method was used. A SCA was

connected to a 2"x 2" Sodium Iodide (NaI) Scintillation probe. NaI is the material of choice when performing gamma scintillation.

This method is generally used for screening materials for ^{226}Ra concentrations and utilizes the principle of secular equilibrium. The ^{226}Ra is determined by measurement of its' daughter ^{214}Bi (Bismuth). ^{214}Bi has a prominent gamma ray at 609.31 KeV with an abundancy of 46%. The window of the SCA is set for gamma energies between 599 KeV and 619 KeV. This allows the 609.31 KeV gamma associated with ^{214}Bi to form at the centroid of the energy window. Assuming secular equilibrium exists, the ^{214}Bi concentration will be equal to the ^{226}Ra concentration.

When dealing with the ^{226}Ra decay chain, a problem can develop when one assumes secular equilibrium. A gaseous daughter, ^{222}Rn (Radon), lies between ^{226}Ra and ^{214}Bi. When the sample material is agitated, such as when preparing the sample for analysis or actually collecting the sample, the gaseous ^{222}Rn is driven off thus destroying the secular equilibrium condition. Because of the short half-life of ^{214}Bi (approximately 20 min.), a rapid reduction in bismuth activity causes severe underestimation of ^{226}Ra concentration if secular equilibrium is assumed. In order for this method to be used with any degree of certainty, an ingrowth period of approximately 28 days is required. This ingrowth period allows for the formation of ^{222}Rn thus reestablishing the secular equilibrium condition.

Portable Exposure Rate Meter

Some licensees are attempting to screen their wastes using a handheld field instrument. This is typically a 1" X 1" NaI detector connected to an exposure rate meter that displays microRoentgen per hour (μR/hr). The roentgen is a unit of radiation exposure which is a measurement of the intensity of the field of radiation to which a person or object is subjected to. The purpose of this instrument is to measure the exposure rate associated with NORM contaminated equipment which is used by most regulating bodies as a criteria for exemption from regulation for that particular piece of equipment. It does not have the ability to discriminate against various gamma ray energies as does the SCA or MCA. Licensees who attempt to use this method for screening wastes do so by measuring the exposure rate radiating through a sample container. If the exposure rate is less than a predetermined level, an assumption is made that the concentration of radioactive material is below regulatory limits.

SAMPLE PREPARATION

Samples were prepared under standard laboratory conditions of cleanliness and contamination control. The samples were placed in 500 ml polyethylene Marinelli beakers and weighed adjusting for beaker weight using predetermined tare weights. The sample weight was recorded and the beaker lids were sealed with tape to minimize the escape of radon gas. The Marinelli beakers were used for all analysis methods to ensure continuity of results. It should be noted that in actual field conditions, the SCA method uses a 1 liter plastic bottle. Because of the different sample geometries, actual comparison of laboratory vs. screening method results could show even greater error associated with the screening method than what is shown in this study.

SAMPLE ANALYSIS

After the samples were prepared, secular equilibrium was allowed to establish. The samples were allowed to stand undisturbed for a minimum of 28 days. The samples were then analyzed using gamma spectroscopy and the two screening methods. A sample holder was constructed for use with SCA method to ensure that sample orientation to the NaI detector remained constant for all samples analyzed. It should be noted that use of the sample holder will produce more accurate results for this study than would be achieved in the field. Results of the analysis are given in Table 1. The data indicates that even after allowing sufficient time to lapse to create a secular equilibrium condition, significant differences between the SCA and gamma spectroscopy (GS) activities exist. In samples with appreciable activity (ie >5 pCi/gm), differences of as much as 46% can be seen (sample # 3606). Part of this difference can be attributed to the fact that the polyethylene containers are not 100% impervious to the radon gas. The gas can diffuse through the plastic thereby reducing the radon and bismuth activity. The only way to totally prevent this would be to seal the sample material in a metal container and allow equilibrium to develop. This would not be practical in most applications. Most states that regulate NORM have set a limit for release for unrestricted use of 5 pCi/gm for wastes and lands. In several samples where GS indicates activity above this limit, the SCA method indicates activities suitable for unrestricted release (sample # 3599, 3605, 3628, 3633, 3639, 3599). This makes the SCA method inappropriate for use when releasing material to the environment.

Some states allow the SCA method to be used when screening materials for determining disposal options. Louisiana allows the disposal of wastes <30 pCi/gm in Commercial Nonhazardous Oilfield Waste Facilities (NOW). Some samples in this study have indicated activities above this limit by GS but the SCA method shows acceptable levels for this disposal option (sample #3601, 3615).

The difference in results between the two methods would be more evident had more sample material been available at the 30 pCi/gm level.

After the samples were analyzed in equilibrium, the sample material was removed from the sample containers and the equilibrium condition was terminated. This was accomplished by placing the sample material on paper plates and stirring the material every two hours for a total of 24 hours. This agitation drove off a majority of the trapped radon gas in the material and partially destroyed the equilibrium condition. A portion of the residual ^{214}Bi was removed through the radioactive decay process after approximately 2.5 hours. The samples were then analyzed using the SCA and GS methods. These results are given in Table 2. A comparison of the data in Table 1 and 2 shows a significant reduction in the ^{214}Bi after the equilibrium was partially destroyed. In some instances, a reduction of as much as 35% was noticed (sample # 3593). Results similar to these should be expected when sampling containerized wastes for the determination of disposal options. In several instances, samples analyzed in secular equilibrium by the SCA method yielded results unacceptable for disposal in NOW facilities or other nonradioactive material disposal sites. These same samples, when analyzed by the SCA method after secular equilibrium was partially destroyed, appear to be acceptable for these disposal options. It should be noted that in both Table 1 and 2, the results for radium by GS did not significantly change.

To more closely show how the SCA method and GS compare under real conditions, sixteen soil samples were collected in the field and placed in typical sample containers (ziplock bags). The samples were returned to the laboratory and prepared using the same methodology as mentioned previously. The samples were then analyzed using the SCA method and GS. This was done in the typical timeframe as is the case with most samples analyzed in the field and sent for commercial analysis (2-5 days from sample collection to analysis by the laboratory). The results are given in Table 3. In many instances it can be seen that regulated material could be mistaken as acceptable material (#3499, 3502, 3504, 3506) when using the SCA results. The samples were then allowed to stand undisturbed for 28 days to allow the establishment of secular equilibrium. The samples were then analyzed using the SCA method and GS. The results of these analysis are given in Table 4. A comparison of the data in these two tables shows a dramatic increase in the ^{214}Bi activity by the SCA method if secular equilibrium is allowed to occur. Results similar to these should be expected when comparing field screening results to those from a commercial laboratory. It can be seen that the SCA method is not acceptable for the determination of regulatory requirements or for the determination of disposal options. It should be noted that the radium results by GS in Table 3 and 4 did not significantly change.

Finally, exposure rates were taken on all samples analyzed during both equilibrium and nonequilibrium conditions. The results can be seen in Tables 1 through 4. Absolutely no comparison can be drawn between exposure rate and concentration. This is due primarily to the varying response of the exposure rate instrument to the varying gamma ray energies present and to varying concentrations of radionuclides and their respective daughter products from sample to sample. This method is not acceptable for screening wastes for radioactivity concentrations and warrants no further discussion.

CONCLUSION

The SCA method is a good screening method for use when trying to determine when more precise laboratory analysis is required. When using the SCA method, if the results are well above regulatory limits it is a relatively safe assumption that the material exceeds those limits. The SCA method is acceptable for use on large projects to determine when release levels are being approached so that samples may be sent to a commercial laboratory for more accurate analysis. The SCA method is not acceptable for use when determining the following:

1) The acceptability of a waste, soil, land, or other material for release for unrestricted use.

2) The determination of whether a material or plot of land is exempt from regulatory requirements.

3) The determination of the proper method of disposal of the waste or material.

4) Whether compliance is required or when classifying wastes for transportation under the Department of Transportation Regulations in 49CFR.

Gamma spectroscopy is the only definitive means for the determination of concentrations of radioactive materials and the classification of wastes for disposal and transportation. It is the only method acceptable to most federal and state agencies for proper determination of radioactive concentrations. By combining the use of the SCA method and GS, licensees can minimize project costs while maintaining regulatory compliance, reducing the possibility of violations and civil penalties, and minimize their overall liability with respect to dealing with hazardous substances.

Table 1.

Sample I.D.	SCA Activity	± 2σ	MDA	GS (Ra-226) Activity	± 2σ	MDA	GS (Bi-214) Activity	± 2σ	MDA	uR/hr
3593	71.01	1.22	0.17	91.49	4.89	1.63	76.86	0.86	0.24	40
3594	20.40	0.58	0.12	29.33	2.16	0.78	24.02	0.35	0.05	22
3595	2.46	0.28	0.10	3.18	0.68	0.24	2.31	0.10	0.02	11
3598	72.97	1.13	0.14	105.23	4.56	1.56	87.46	0.76	0.12	70
3599	4.70	0.39	0.13	5.63	1.71	0.53	4.01	0.22	0.08	12
3601	29.77	0.74	0.14	46.78	2.75	0.95	39.57	0.52	0.07	25
3605	3.74	0.37	0.13	7.05	0.82	0.27	4.69	0.16	0.02	12
3606	11.30	0.43	0.10	20.85	1.67	0.62	16.98	0.28	0.04	18
3609	150.87	1.92	0.21	215.12	11.36	2.66	176.28	1.33	0.19	80
3615	20.69	0.60	0.12	35.05	2.28	0.84	28.90	0.38	0.05	24
3626	17.89	0.58	0.13	28.00	2.70	0.82	23.37	0.35	0.05	26
3628	2.87	0.32	0.11	6.70	1.35	0.37	4.31	0.17	0.03	10
3633	4.06	0.41	0.13	6.52	0.93	0.29	4.82	0.17	0.02	12
3634	36.06	0.82	0.14	60.96	3.77	1.10	48.17	0.57	0.08	25
3635	36.48	1.03	0.21	52.85	3.02	1.21	43.32	0.63	0.09	20
3639	3.78	0.38	0.13	5.65	0.60	0.29	3.54	0.14	0.02	10
3642	39.50	0.78	0.12	59.76	3.00	0.95	49.56	0.52	0.07	34

Table 2.

Sample I.D.	SCA Activity	± 2σ	MDA	GS (Ra-226) Activity	± 2σ	MDA	GS (Bi-214) Activity	± 2σ	MDA	uR/hr
3593	46.21	1.01	0.17	90.87	5.13	1.63	71.65	0.91	0.14	35
3594	16.90	0.54	0.12	28.50	2.38	0.74	21.98	0.37	0.06	22
3595	1.01	0.25	0.10	3.26	0.56	0.22	1.98	0.10	0.02	14
3598	60.44	1.04	0.14	101.85	4.52	1.53	78.66	0.77	0.12	45
3599	2.30	0.35	0.13	5.33	1.73	0.43	3.64	0.21	0.04	13
3601	27.00	0.71	0.14	43.03	2.13	0.80	36.76	0.51	0.07	30
3605	1.29	0.32	0.13	5.43	0.96	0.38	3.60	0.19	0.03	12
3606	12.07	0.44	0.10	27.11	1.30	0.73	19.34	0.31	0.17	21
3609	103.55	1.61	0.21	184.40	7.39	2.49	146.31	1.26	0.19	65
3615	20.37	0.59	0.12	68.46	4.15	1.42	58.26	0.57	0.10	26
3626	17.19	0.57	0.13	30.25	2.30	0.85	23.91	0.38	0.06	23
3628	3.87	0.34	0.11	8.38	0.96	0.37	5.67	0.17	0.03	15
3633	2.83	0.36	0.13	6.74	1.43	0.41	4.28	0.16	0.03	13
3634	27.36	0.73	0.14	54.20	3.30	1.04	41.43	0.58	0.08	28
3635	23.66	0.87	0.21	47.68	4.12	1.37	36.27	0.67	0.09	23
3639	2.09	0.34	0.13	5.80	1.60	0.37	3.15	0.15	0.02	12
3642	33.26	0.72	0.12	60.52	3.47	1.04	48.95	0.53	0.08	34

Table 3.

Sample I.D.	SCA Activity	± 2σ	MDA	GS (Ra-226) Activity	± 2σ	MDA	GS (Bi-214) Activity	± 2σ	MDA	uR/hr
3497	15.07	1.03	0.32	22.23	2.93	1.83	16.07	0.52	0.16	16
3498	0.37	1.04	0.46	<0.87	N/A	0.87	1.18	0.17	0.08	10
3499	23.88	1.39	0.41	34.35	4.55	2.57	26.55	0.71	0.22	15
3500	42.69	0.82	0.11	60.63	3.47	1.89	29.50	0.57	0.16	43
3501	21.55	0.59	0.11	26.97	2.28	1.37	21.05	0.34	0.10	25
3502	26.39	0.99	0.24	38.90	2.92	1.89	29.50	0.57	0.16	18
3503	0.35	0.90	0.41	<0.62	N/A	0.62	0.62	0.12	0.07	12
3504	2.77	1.14	0.48	5.24	1.90	1.25	3.66	0.31	0.12	10
3505	0.49	1.10	0.49	4.49	1.42	1.10	2.56	0.28	0.12	10
3506	18.47	1.11	0.33	30.11	3.29	2.09	21.79	0.58	0.18	13
3507	41.21	1.53	0.36	58.91	5.19	3.23	46.25	0.93	0.25	18
3509	-0.07	0.71	0.32	1.37	0.74	0.63	1.00	0.12	0.06	10
3510	0.49	1.37	0.61	4.53	2.24	1.29	2.55	0.27	0.10	10
3511	-0.56	1.46	0.66	<1.02	N/A	1.02	0.56	0.14	0.10	10
3512	-3.53	0.96	0.47	3.85	1.75	0.96	1.59	0.22	0.10	10
3514	1.20	0.90	0.39	1.55	1.05	0.73	1.19	0.17	0.08	10

Table 4.

Sample I.D.	SCA Activity	± 2σ	MDA	GS (Ra-226) Activity	± 2σ	MDA	GS (Bi-214) Activity	± 2σ	MDA	uR/hr
3497	17.65	1.07	0.32	20.64	3.01	1.09	16.61	0.50	0.07	15
3498	4.87	1.15	0.46	2.40	1.42	0.58	1.10	0.17	0.05	12
3499	33.89	1.54	0.41	40.48	5.81	1.49	28.25	0.74	0.11	18
3500	56.18	0.89	0.11	62.26	3.21	1.13	52.72	0.52	0.08	49
3501	25.64	0.63	0.11	24.81	1.67	0.70	21.91	0.37	0.06	28
3502	28.93	1.04	0.24	37.64	3.58	1.17	30.05	0.59	0.08	18
3503	0.84	0.93	0.41	<0.40	N/A	0.40	0.51	0.11	0.03	10
3504	8.02	1.26	0.48	5.84	1.59	0.62	3.55	0.29	0.06	12
3505	5.94	1.23	0.49	4.91	1.55	0.63	2.87	0.29	0.06	10
3506	25.00	1.21	0.33	32.89	4.20	1.39	23.21	0.58	0.09	16
3507	52.47	1.67	0.36	64.33	6.06	1.86	50.12	0.88	0.13	18
3509	2.23	0.77	0.32	<0.41	N/A	0.41	0.97	0.15	0.04	10
3510	5.39	1.49	0.61	4.84	1.29	0.75	2.58	0.29	0.07	10
3511	5.15	1.59	0.66	<0.46	N/A	0.46	0.32	0.11	0.04	10
3512	2.04	1.11	0.50	<0.44	N/A	0.44	1.42	0.20	0.05	10
3514	3.86	0.96	0..39	2.55	0.82	0.38	1.16	0.15	0.04	12

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A Health-Based Approach to

The Regulation of

Naturally Occurring Radioactive Materials

By

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This paper describes the process leading to the adoption of Mississippi State Oil and Gas Board Rule 69, which governs oilfield naturally occurring radioactive materials (NORM). Oilfield NORM litigation in Mississippi is widespread. Thus, the adoption of new regulations was highly publicized around the state. This paper first describes the proceedings before the Oil and Gas Board, with a detailed description of the physicians and scientists who testified for the proponents and the opponents of proposed Rule 69. This paper then analyzes the final version of Rule 69, with particular emphasis on responsibility of the oil production companies. Unlike any other regulations governing oilfield NORM in the country, Mississippi's Rule 69 is a health-based approach with a framework that is implementable by oil production companies without outside scientific assistance.

INTRODUCTION

The purpose of this paper is two-fold. First, this paper will tell a war story--the story about Mississippi State Oil and Gas Board Rule 69, from its inception to its passage. Next, the paper will analyze Rule 69 and describe what is now required of oil field operators.

THE BEGINNING

In 1995, the Mississippi legislature removed jurisdiction over oil field NORM (naturally occurring radioactive material) from the Department of Health and vested exclusive jurisdiction in the State Oil and Gas Board. The enabling legislation reads:

> Notwithstanding any other provision contained in the laws of the State of Mississippi, the Board shall have exclusive jurisdiction and authority, and it shall be its duty to make, after notice and hearing is hereinafter provided, such reasonable rules, regulations, standards and orders, and to issue such permits as may be necessary, to regulate the use, management, manufacture, production, ownership, investigation, and non-commercial disposal of oil field exploration and production wastes in order to prevent, eliminate, or reduce wastes by pollution to acceptable levels in order to protect the public health, safety and the environment.

Miss. Code Ann. § 53-1-17(7)(Supp. 1995). "Oil field exploration and production wastes" is defined, among other things, as "naturally occurring radioactive." Miss. Code Ann. § 53-1-3(2)(t)(i)(Supp. 1995).

With the legislature's directive to the Oil and Gas Board to adopt new NORM regulations, Mid-Continent Oil and Gas Association convened a group of experts to draft a proposed rule for submission to the Oil and Gas Board.

The group included legal advisors, health physicists, and industry representatives. The groups' goal consisted of six basic elements:

- Regulations should control "real" rather than "perceived" threats to human health.
- The definition of NORM for regulatory purposes should be clear.
- The Mississippi State Oil and Gas Board should administer a NORM regulation program.
- The regulations must be consistent with existing radiation protection standards.
- A risk-based approach to regulation should be implemented.
- Regulations must be implementable by those who are subject to its provisions.

After several months of preparation, the first draft of what would become Rule 69 was finalized and submitted to the Oil and Gas Board. Shortly thereafter in September of 1995, the Board officially proposed Rule 69.

THE OPPOSITION COMES TO TOWN

Shortly after the Board proposed Rule 69, a group of thirty contestants filed a Notice of Contest with the Board. The contestants were represented by Sacks and Smith, a New Orleans law firm that represents many plaintiffs in pending NORM litigation. In their first procedural move before the Board, the contestants filed a Motion to Dismiss Proposed Rule 69 and a Motion for Interim Adoption of the Regulations for the Control of Radiation in Mississippi, which are the former Department of Health Regulations regarding oil field NORM. The contestants alleged in their Motion to

Dismiss that the Board had not received approval from the Mississippi Department of Environmental Quality which, according to the contestants, was required by state law. Further, contestants argued that the Board violated Mississippi law by not preparing an economic impact statement.

A group of supporters of proposed Rule 69, Fina Oil and Chemical Company, Vintage Petroleum, Inc., and Osborn Heirs Company (hereinafter "Supporters"), filed a Brief in Support of Rule 69 and In Opposition of Contestants Motion to Dismiss. The Supporters argued that the enabling legislation gave "exclusive" jurisdiction to the State Oil and Gas Board in regulating NORM. Resorting to the definition of "exclusive" from Webster's Dictionary--"not shared with others"--the Supporters argued that the Board was not required to seek approval with the Department of Environmental Quality before promulgating Rule 69. Further, the Supporters argued that Mississippi law does not require an economic impact statement for "any rule which is expressly required by state law." Miss. Code Ann. § 25-45-6(4)(b)(Supp. 1995).

From the "bench" the Board denied contestant's Motion to Dismiss Proposed Rule 69. The Board also denied contestant's Motion for Interim Adoption of the Regulations for Control of Radiation in Mississippi.

THE FORUM MOVES TO THE CHANCERY COURT

In late November of 1995, nine of the previous thirty contestants filed a Petition for Perpetuation of Testimony in the Hinds County Chancery Court. The suit named the following parties as Defendants:

> the individual members of the State Oil and Gas Board;
> The State Oil and Gas Board;
> Mid-Continent Oil and Gas Association;
> Fina Oil and Chemical Company; and
> Vintage Petroleum, Inc.

The Petition requested that the chancery judge issue an order "allowing them to depose by oral examination and written interrogatories" the named Defendants.

The Defendants filed a Motion to Dismiss the Petition relying heavily on State Oil and Gas Board v. McGowan, 542 So.2d 244, 249 (Miss. 1989). In McGowan, the Plaintiff had also filed suit in chancery court requesting discovery before the Oil and Gas Board took action on a pending matter. Id. The Supreme Court held:

> Judicial review may be had of any final rule, regulation or order of the Board. Prior to an appeal from a final rule, regulation or order, as contemplated by the statute, the chancery court has no jurisdiction to participate in the administrative process and it was error to do so when the effect amounted to an intervention in a pending proceeding.

Id.

After a hearing on the matter, Judge Patricia Wise issued an Opinion dismissing the Petition. The Court noted "until the administrative process is exhausted, the Mississippi Supreme Court requires that the petitioners herein

be governed by and limited to the procedures for hearings as set for in the Board's rules."

PROPOSED RULE 69 CHANGES FORM

Unbeknownst to any of the parties, the Board hired a consulting expert, Vern Rogers of Rogers & Associates in Utah, to review proposed Rule 69. Mr. Rogers did indeed review the Rule and made several substantive changes. The Board re-proposed Rule 69 with Mr. Rogers' changes. The revised Rule 69 was similar to the original version of Rule 69 with the following exceptions: (1) the property release criteria were lowered to reflect NORM concentrations in soil that were lower than that permitted by the Mississippi Department of Radiological Health; (2) the property release criteria were to be based upon the maximum ambient gamma exposure rate measured at a height of 0.3 meters above the ground for each one meter grid square; (3) the property release criteria include subsurface measurements made to a depth of one meter and at least five boreholes per acre, with a minimum of three boreholes per site; (4) equipment release criteria were general less restrictive than those contained in the original version of the Rule; and (5) definitions were changed somewhat to accommodate wording modifications to the original version of the Rule.

FINALLY, THE TRIAL

The Board proposed Rule 69 in September of 1995. After many continuances and other procedural delays, the trial was finally set for April 2, 1996.

Three different factions presented evidence to the Board. Onetta Whitley of the Attorney General's Office presented the Oil and Gas Board's case in support of the latest version of Proposed Rule 69, which incorporated Vern Rogers' alterations. Jeff Reynolds presented Fina, Vintage and Osborn Heir's case in support of Rule 69 as originally drafted. Stuart Smith and David Cobb presented evidence on behalf of the contestants in opposition to both Rules.

THE OIL AND GAS BOARD STAFF'S CASE

On the first day of trial, the staff presented their evidence in support of the revised version of Proposed Rule 69. The staff called Dr. Vern Rogers as their only witness. Dr. Rogers testified that the Rule was environmentally and scientifically sound and posed no health threat to the members of the general public or oil field workers. Further, Dr. Rogers testified in support of his proposed changes.

THE SUPPORTERS OF ORIGINAL RULE 69

The Supporters of the original proposed Rule 69 presented evidence through three witnesses. Carol Berger, the driving force behind the drafting

of the original Rule 69, testified that Rule 69 in its original version or the current proposed Rule 69 would pose no health effects to the general public or workers in oil fields. Ms. Berger is a Board Certified Health Physicist, a profession that deals primarily with the effects of radiation on the human body.

Dr. Tate Thigpen, a Board Certified Oncologist and Director of Oncology at University Medical Center in Jackson, also testified on behalf of the Supporters of proposed Rule 69. Dr. Thigpen testified that no study has ever shown any adverse effect from radiation exposure at levels of 50,000 millirem or below. The standard of proposed Rule 69 insures exposure of less than 100 millirem. Dr. Thigpen testified that a conservative estimate of exposure rates that could cause adverse health effects is 10,000-20,000 millirem. Dr. Thigpen gave an example of the radiation doses that he uses regularly to treat breast cancer patients. The exposure rate of the treatment is thousands of times higher than the standard as set by Rule 69.

Next, Dr. John Scott, head of Nuclear Medicine for the Veterans Administration in the Southeast, also testified on behalf of the Supporters of Rule 69. Dr. Scott echoed the fact that no study had showed adverse health effects from exposure to radiation at less than 50,000 millirem. Dr. Scott gave an example of radiation levels that are administered as treatment to certain patients. The radiation doses Dr. Scott described are thousands of times higher than that of proposed Rule 69.

THE CONTESTANTS' CASE

At the outset of the trial, the Supporters of original Rule 69 filed a Motion in Limine seeking to exclude all of the contestants' experts from testifying. The Board reserved ruling on the Motion in Limine until each witness was questioned on *voir dire*. All of the contestants' experts were against the adoption of any form of Rule 69. The experts apparently supported the Department of Health regulations, Section N of the Regulations for Control of Radiation in Mississippi. Section N governs all NORM and is not limited to NORM in the oil field. Section N created a regulatory scheme that was difficult to understand and very expensive to implement.

The contestants first called Dr. Marvin Resnikoff of New York, New York, as an expert in health physics and environmental science. On *voir dire*, Dr. Resnikoff admitted he failed the board certification exam for health physics. The supporters also questioned Dr. Resnikoff on his book, *Living Without Landfills.* The National Council on Radiation Protection reviewed Mr. Resnikoff's book and found as follows:

> We find the report is misleading for the following reasons:
>
> 1. relevant information is excluded;
> 2. there are misstatements of fact;
> 3. it contains many exaggerations and exhibits bias; and
> 4. there are many instances of faulty logic.

Furthermore, the Nuclear Regulatory Commission reviewed Dr. Resnikoff's book as follows:

> We . . . believe that the final report continues to contain a large number of inaccurate and incomplete statements which lead to inappropriate conclusions and recommendations.

After *voir dire*, the Board allowed Dr. Resnikoff to testify, although Chairman Zuccaro stated that the Board had serious misgivings about the qualifications of Dr. Resnikoff.

The contestants next called Mr. Peter McDowell as an expert in the area of property evaluation and insurance issues. Although the Supporters objected on relevance grounds, the Board allowed Mr. McDowell to testify, but only as a fact witness, not to his opinions.

The contestants called Andrew Gross as an expert in health physics, clean up assessment and regulatory compliance. On *voir dire*, Mr. Gross admitted he did not have an undergraduate degree. Further, Mr. Gross admitted he had never written any peer reviewed articles published in a scientific journal. Mr. Gross had presented a paper in a seminar only two years ago in which he stated "the low levels of gamma ray radiation associated with the oil and gas industry are almost always not a hazard." Mr. Gross was excluded from testifying as an expert.

RULE 69

On April 19, 1996, the Board issued an order adopting Rule 69. A copy of the Order and Rule are attached as Appendix "A." The Rule, as adopted, was essentially the original version of Rule 69 without many of Vern Rogers' alterations. The Board made one substantial alteration to the original

version of the Rule--the provision allowing land farming as a remediation procedure was omitted. The only testimony presented to the Board indicated that land farming was an environmentally safe remediation option. Vern Rogers testified that he omitted the land farming provisions in his revision of the Rule because he felt that the land farming provisions belonged in Rule 68 rather than Rule 69. However, Dr. Rogers testified that under the provisions of Rule 69, the Board could consider land farming on a case-by-case basis. Dr. Rogers has previously published a paper listing land farming as a disposal option. See Rogers & Associates, Management and Disposal Alternatives for NORM Wastes in Oil Production and Gas Plant Equipment, May 1990.

A. Scope of Rule 69

The application of Rule 69 (and the Board's jurisdiction over NORM) is limited to oil and gas production facilities which were permitted by the Oil and Gas Board after July 1, 1995 and were active or properly reported as inactive after July 1, 1995. The Rule does not apply to facilities which were abandoned prior to July 1, 1995. Those sites abandoned prior to July 1, 1995, "and/or not permitted by the Oil and Gas Board will continue to be regulated in the manner in which the sites were regulated prior to July 1, 1995," which means they will be regulated under the Department of Health Rule. Rule 69, Plaintiff 1(d).

B. Standard of Rule 69

Under Rule 69, oil field exploration and production sites will be operated and released in a manner that insures a total estimated dose equivalent (TEDE) of less than 100 millirem per calendar year for workers and members of the general public. If operators follow the criteria, as set forth below, they will comply with the standard. If the TEDE exceeds 100 millirems in a calendar year, the facility falls under the jurisdiction of the Department of Health.

C. Surveys

If a radiological survey has not been performed at a location site, Rule 69 mandates that the survey shall be performed within one year of the effective date of Rule 69, which is June 1, 1996. For wells permitted after the effective date of Rule 69, the initial survey shall be performed prior to the start of exploration/production operations and again, two years after the start of exploration/production operations. After the initial survey, surveys shall be performed every five years during exploration/production activities if the maximum exposure rate recorded in the last survey exceeds 50 microR per hour above background. Otherwise, the surveys must be performed every ten years. Surveys shall also be performed "as necessary" to evaluate radiological conditions in the event of any equipment repairs, equipment maintenance, site maintenance, accident or spills, if any of these results in a release of production scales or sludges onto the surface.

Operators must perform surveys to evaluate the magnitude of exposure rates above ground surfaces and in the vicinity of equipment. The ground surface surveys must report the maximum readings for each one meter by one meter grid area over the well head, tank battery site, heater/treater site, all surface pipe areas and other areas of the location site where contamination is likely to occur. Otherwise, the survey must report the maximum readings for each ten by ten meter grid. The survey results must be documented on Board Form No. 21 or its equivalent.

D. Criteria for Site Operations

If an exploration/production site exceeds exposure rates of 250 microR per hour above background, Caution Signs must be posted at the perimeter of the property. The Caution Sign shall have the words "Caution--N.O.R.M.--Potential Health Risks" and "No Trespassing--Authorized Personnel Only." Sites with exposure rates exceeding 700 microR per hour above background shall be fenced with Caution Signs on the fence. Sites with exposure rates exceeding 5,000 microR per hour above background shall be fenced with Caution Signs and other signs as required by the Department of Health.

E. Site Maintenance

Maintenance activities at sites with a maximum exposure rate of less than 50 microR per hour above background shall require no controls. If the exposure rate exceeds 50 microR per hour, maintenance workers must use dust masks, water sprays or other dust control methods. Land or equipment

maintenance that may cause workers to exceed 100 millirems TEDE in a calendar year falls under the jurisdiction of the Department of Health.

F. Release of Property

Property can be transferred to another producer without regard to the radiation levels on the property. The seller must provide the buyer with the most recent radiation survey.

A site may be released for unrestricted use if radiation levels do not exceed 50 microR per hour above background (measured at one meter above the ground) at any point on the location and a borehole survey indicates a maximum exposure rate of less than 200 microR per hour including background. The borehole survey must report at least five boreholes per acre, with a minimum of three boreholes per site. At least one of the boreholes shall be drilled at the location of the maximum surface exposure rate measurement. The boreholes must be at least one meter deep and must be measured at .15 meter intervals.

In order to achieve the release criteria, an operator may remediate by transferring soil to a radioactive material storage area under Rule 68 or other remedial actions as approved by the Board.

G. Criteria for Release of Equipment

Equipment may be transferred to another producer without regard to radiation levels. In order to be released for unrestricted use, the equipment must exhibit a surface disintegration rate of less than 2,000 DPM per 100

centimeters squared above background and exhibit an exposure rate of less than 25 microR per hour at a distance of 2.5 centimeters from the equipment surface,.

H. Records Operators Must Keep

Survey records, instrument calibration records, material transfer records and records setting forth the qualifications of the radiation survey. These records must be maintained by the operator for a minimum of ten years after a property has been released from unrestricted use.

I. Exceptions

Rule 69 specifically states that exceptions to the Rule may be allowed upon good cause shown and proper notice and hearing of a petition filed with the Board.

CONCLUSION

Rule 69 is a first. It is the first regulation in the United States that was promulgated to deal exclusively with oil field NORM. It is also the first health-based radiation regulation in the country. Though it was a long haul, the NORM regulations now governing this state are easily implementable by the parties most affected by them. The contestants have appealed the Oil and Gas Board's adoption of Rule 69. The appeal is currently pending.

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State Oil and Gas Board

State of Mississippi

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STATE OIL AND GAS BOARD
W. R. Lewis, Supervisor

BEFORE THE STATE OIL AND GAS BOARD

STATE OF MISSISSIPPI

IN RE: DOCKET NO. 226-95
ON THE BOARD'S OWN MOTION TO
CONSIDER ADOPTING RULE 69
CONTROL OF OIL FIELD NATURALLY
OCCURRING RADIOACTIVE MATERIALS
(NORM)

O R D E R NO. 73-96

THIS DAY this cause came on for hearing before the State Oil and Gas Board on the Board's own motion to consider the adoption of proposed Statewide Rule 69 - Control of Oil Field Naturally Occurring Radioactive Materials (NORM); said hearing being called for such purpose; and

The Board finding that due, proper and legal notice of the meeting of the Board for the purpose of considering and taking action with respect to such matter was given in the manner and way provided by law and the rules and regulations of the Board; that due, legal and sufficient proofs of publication are on file with the Board; and that the Board has full jurisdiction of the subject matter to hear and determine same; and

WHEREAS, pursuant to said notice given, public hearing was held by said Board in the Hearing Room, Suite E, 500 Greymont Avenue, Jackson, Mississippi, commencing at 9:00 a.m. on April 2, 1996, and ending at 5:00 p.m., April 4, 1996, at which hearing all

persons present who desired to be heard on said matter were heard and all testimony and evidence were duly considered by those present at said meeting; and

WHEREAS, the Board has fully considered said matter and the evidence and recommendations made in said hearing and finds as follows:

1. The Mississippi Oil and Gas Board (hereinafter "the Board") has been charged by the Mississippi Legislature with making regulations for the control of oil field naturally occurring radioactive materials (hereinafter "NORM") to ensure that radiation exposures of workers and members of the general public resulting from NORM are prevented, eliminated or reduced to acceptable levels in order to protect the public health, safety and environment. The Board finds that there is substantial evidence in the record before it to support the following findings.

2. The appropriate analysis in developing such regulations should utilize the health criteria established by the Mississippi Department of Health, which limits annual doses to workers and the general public to 100 millirem per year (mrem/y). Such an analysis should also be based upon different scenarios for multi-pathway radiation exposures to oil field workers and the general public.

3. NORM is found in rocks, soil, plants, animals, water and air throughout the environment. Soil and rocks contain the highest concentrations. Radium isotopes ^{226}Ra and ^{228}Ra are the primary concern in NORM associated with oil field operations. When oil and gas production fluids are brought from underground formations to surface equipment, they carry traces of dissolved radium, the most soluble element in the uranium and thorium decay chains. The radium tends to precipitate in the scales and sludges which, over time, accumulate in tubes, separators, and other surface equipment as the temperature, pressure, and chemistry of the fluids change. The radium occasionally accumulates to exceed background levels. Radon, an inert gas in the uranium decay chain, is also brought to the surface with natural gas production streams. Both the radium and radon isotopes soon produce equilibrium concentrations of their decay products. Since radium and its decay products are readily detectable even at natural background levels, slight to moderate elevations are often observed in oil field operations.

4. The levels of potential radiation exposure contemplated by the rule adopted by this Board have been set and established by evaluation of substantial scientific testimony. The Board finds the testimony presented by Dr. Vern Rogers and Ms. Carol D. Berger, CHP, to be particularly convincing and credible. Dr. Rogers and Ms. Berger testified as to the levels of exposure to radioactive materials one can expect in an oil field setting and as to a framework for a reasonable means of regulating NORM so as to achieve the goal of ensuring that radiation exposures to oil field workers and members of the general public resulting from NORM are prevented, eliminated or reduced to acceptable levels.

5. Further, the Board finds the testimony of Dr. Tate Thigpen and Dr. John W. Scott instructive and compelling. Scientific testimony offered by them regarding the levels of radiation and degrees, doses and levels at which medically observable health hazards exist has provided the Board with empirical data upon which to found its ruling.

Dr. Thigpen and Dr. Scott both offered testimony based upon years of experience in the medical field. Dr. Scott, an established specialist in nuclear medicine, testified to the negligible adverse health effects observed from administering high doses of radiation in a variety of nuclear medical procedures. The dose levels routinely used in nuclear medicine treatment are often thousands of times greater than those exposure levels contemplated under Rule 69.

In addition, the testimony of Dr. Thigpen, a board certified oncologist at the University Medical Center, was equally compelling. Dr. Thigpen testified regarding similar medical treatment using high levels of radiation. Dr. Thigpen testified that scientific studies have not demonstrated any observable adverse health effects below a dose of 50,000 millirem. Dr. Thigpen testified that a very consecutive level below which adverse health effects are medically insignificant would be 10,000 to 20,000 millirem. Dr. Scott also testified as to this. The Board recognizes Dr. Thigpen's and Dr. Scott's conservative levels and finds that the 100 mrem/y maximum exposure levels contemplated in Rule 69 is a scientifically and medically conservative level which will provide protection for the citizens of Mississippi regardless of age from any harmful exposure to radioactive materials.

The Board further finds that the testimony of Drs. Scott and Thigpen is the only credible medical testimony addressing concerns and issues raised by the rule as to the impact

and effects the rule's maximum allowable levels would have.

6. The Board finds that it should accept and adopt the same goal for the protection of the health and safety of the public as has been established by the Mississippi State Department of Health's Division of Radiological Health (hereinafter "MDRH"). MDRH uses a primary radiation exposure limit of 100 mrem/y (1 mSv/y) total effective dose equivalent to members of the general public from man-made sources. The MDRH has held that this limit should not be exceeded by oil field NORM. The 100 mrem/y limit is identical to that set by the U. S. Nuclear Regulatory Commission for continuous exposures. It is also similar to that recommended by the National Council on Radiation Protection and Measurements (NCRP), except that the NCRP limit excludes radon contributions.

7. Higher radiation doses are generally permitted for infrequent exposures and for workers who are exposed as part of their employment. The NCRP limits allow up to 500 mrem/y for infrequent exposures on the assumption that this dose would not be sustained for extended periods for the same individuals. The NCRP gives the same guidance for radiation from NORM, allowing up to 500 mrem/y for infrequent exposures but only 100 mrem/y for continuous exposures. The U. S. Nuclear Regulatory Commission permits up to 5,000 mrem/y exposures for badged radiation workers, up to 500 mrem/y for workers not under a personal radiation monitoring program, and up to 2 mrem/h for doses from external sources in an unrestricted area. The MDRH uses equivalent standards as Mississippi is an "agreement state".

8. Oil field NORM can potentially expose different individuals to different radiation doses that vary widely. These radiation doses depend mainly on the NORM concentration, its configuration in soil, equipment, and other environmental media, the proximity of individuals being exposed, and the length of time the individuals are exposed. It is reasonable to consider four scenarios for NORM exposure: (1) an oil field operations worker, (2) an oil field maintenance worker, (3) a casual visitor to an uncontrolled oil field site, and (4) the resident of a house built at a former oil field site.

9. The oil field operations worker, maintenance worker, and casual visitor are all exposed to gamma radiation from NORM scale contamination in the site soil and from the

NORM scale and sludge inside the oil field equipment. It is reasonable to assume that the operations worker will spend 500 hours per year at the site (or equivalent sites), based on two hours per day, five days per week, 50 weeks per year. The maintenance worker can reasonably be assumed to spend 1,000 hours per year at the site (or equivalent sites), based on four hours per day, five days per week, 50 weeks per year. The casual visitor can reasonably be assumed to spend 300 hours per year at the site (or equivalent sites), based on 1 hour per day, six days per week, 50 weeks per year. Half of the site time for each of these individuals can reasonably be assumed to be spent in close enough proximity to NORM-contaminated equipment to receive equipment-related gamma radiation exposures. Each individual can also be assumed to inadvertently inhale dust and ingest small quantities of surface soil from the site in proportion to the amount of time they spend there.

10. The site resident is exposed to gamma radiation from the site soil, but not from equipment, which will have been removed prior to his or her occupancy. The resident is assumed to spend 700 hours per year outdoors at the site (2 hours x 7 days x 50 weeks) and 6300 hours per year indoors (18 hours x 7 days x 50 weeks) at the site. While the house provides some gamma shielding, it still permits incremental gamma exposure from the surface soil NORM layer. The resident also inhales radon in his or her house that is incrementally higher because of the surface soil NORM-contaminated layer. While outdoors, the resident inadvertently inhales dust and ingests soil from the surface NORM layer. In addition, part of the food he or she consumes can be assumed to have been produced on the site and would, therefore, contain incremental NORM concentrations.

11. External gamma doses can be calculated with the MICROSHIELD computer code. Internal radiation doses from dust inhalation, soil ingestion, and food ingestion can be assessed using the RESRAD computer code. The RAETRAD computer code can be used to analyze exposures from indoor radon inhalation. These computer codes are widely accepted as reliable and accurate predictors of radiation doses.

12. Using these computer codes, one can arrive at an expected radiation dose to the operations worker of 100 mrem/y, the maximum dose acceptable for members of the general

public. That dose would be dominated by gamma radiation from outdoor soil, with less than 10 percent coming from the oil field equipment. The corresponding total dose expected for the maintenance worker may exceed 100 mrem/y because of his or her greater time at the site and more direct exposure to NORM. Therefore, such a worker may be subject to regulation by MDRH unless his or her hours are reduced below these assumed levels or other steps are taken to reduce his or her exposure. The worker's dose would also be dominated by gamma radiation from outdoor soil, but over 20 percent would come from the oil field equipment in this case. Radon inhalation by the maintenance worker would account for less than 5 percent of his or her dose, and soil ingestion and dust inhalation together would also account for less than 5 percent.

13. The expected dose to the visitor (60 mrem/y) would be well below that for the operations worker because of the shorter time a visitor would spend at the site and the shielding by equipment walls. The visitor's dose distribution would be similar to that of the operations worker except that it should be scaled to shorter exposure times. Exposures by the dust inhalation and soil ingestion pathways would be relatively small in all of the scenarios.

14. The dose to the resident would be dominated (48 percent) by gamma radiation through the floor and walls while indoors. Gamma doses while outdoors would add almost another 20 percent, while indoor radon inhalation would contribute nearly 23 percent of the resident's total dose. Dust inhalation and soil ingestion would again be small, totaling less than 2 percent of the resident's dose. Food ingestion would account for the remaining 7 percent.

15. Based on the 100 mrem/y dose estimated for the active site operations worker, and the smaller dose for the visitor, a site could reasonably be left in an unrestricted condition during operations unless excessive radiation levels are noted. Routine surveys should be performed to identify elevated radiation from NORM, and where necessary, warning signs should be used to indicate the presence of NORM. Further, when releasing a site for unrestricted use, it should be surveyed to ensure residual contamination on the surface and at depth are at acceptably low levels. Furthermore, the survey should be transmitted to the site owner. In making the surveys the surface gamma exposure rate should be less than 50

microR/hr and the external exposure rate from surveys in 3-foot deep boreholes should be less than 200 microR/hr. The gamma radiation limit in the boreholes is based on a correlation constant of 10 microR/hour gamma exposure per pCi/g of total radium in the soil.

16. The Board bases these findings on the evidence presented at hearing and the comments made to the Board by interested parties both in writing and in person at the hearing. While some evidence offered by the Contestants, including testimony from Mr. Andrew Gross, was excluded by the Board in response to objections, all such evidence which was proffered into the record was, in fact, considered by the Board in reaching these findings and in adopting the subject rule.

THEREFORE, in light of these findings, it is ORDERED AND ADJUDGED that the Board adopts the following Statewide Rule 69 for the control of oil field NORM:

RULE 69. CONTROL OF OIL FIELD NATURALLY OCCURRING RADIOACTIVE MATERIALS (NORM)

1. Purpose and Scope

   a. This rule provides regulations for control of oil field NORM to ensure that radiation exposures of workers and members of the general public resulting from oil field NORM are prevented, eliminated or reduced to acceptable levels in order to protect the public health, safety and environment.

   b. No person shall receive, possess, use, transfer, own or acquire NORM as defined herein except as authorized in this section or as otherwise provided by State and Federal Regulations.

   c. This rule applies to NORM that has been derived from the exploration and production activities of oil and gas operations within the territorial area of the State of Mississippi at oil and gas production facilities which, on or after July 1, 1995, were properly permitted by the Oil & Gas Board and which, on or after July 1, 1995, were active or properly reported as inactive on Oil & Gas Board Form 9-A.

   d. It is the understanding of the Oil & Gas Board that the intent of the legislature is that location sites surrounding oil and gas production facilities which were abandoned prior to July 1, 1995 and/or not permitted by the Oil & Gas Board will continue to be regulated in the manner in which such sites were regulated prior to July 1, 1995.

2. Definitions

   a. 29 CFR 1910 - Department of Labor, Title 29, Code of Federal Regulations, Section 1910.96, "Ionizing Radiation".

   b. 49 CFR - Department of Transportation, Title 49, Code of Federal Regulations, Subchapter C, "Hazardous Materials Regulations".

c. Accessible Locations - Locations and areas at an exploration/production facility that can be readily occupied by a human.

d. Activity - Disintegration rate of a radioactive material stated in dps, becquerels, μCi, nCi, pCi, or other acceptable units.

e. ANSI-N323 - American National Standards Institute, ANSI-N323-1978, "Radiation Instrumentation Test and Calibration", 1978.

f. Approval - An act of endorsing or adding positive authorization or both.

g. Background - the ambient radiation field to which we are exposed daily, originating from cosmic rays, naturally-occurring radionuclides (^{40}K, etc.) and human endeavors (fallout, fuel cycle, etc.). This radiation field is variable and causes a survey meter to respond in the absence of NORM.

h. Board - The State Oil and Gas Board.

i. Caution Sign - Caution signs shall have the words "Caution - N.O.R.M. - Potential Health Risk" on the upper panel in three (3) inch upper-case yellow letters on a black background, and the words "No Trespassing - Authorized Personnel Only" on the lower panel in two (2) inch upper-case black letters on a yellow background.

j. Detector - A material or device that is sensitive to radiation and can produce a response signal suitable for measurement or analysis. A detector coupled to a ratemeter forms a radiation detection instrument.

k. Exploration/Production Site or Facility - A location where oil and/or gas production activities occur.

l. Exposure Rate - An indication of the potential for a human to incur a radiation dose. Exposure rates are measured in units of "microroentgen per hour" at a height of one meter (three feet) above a horizontal land surface and 0.3 meter (one foot) from the midpoint of a horizontal or vertical equipment surface. A microR meter with an internal or external probe is generally used for this measurement. For unrestricted release of equipment, the rates shall be measured at a distance of 2.5 centimeters (one inch) from the equipment surface.

m. Equipment - Tanks, valves, tubing, rods, pumps, tools, and other equipment commonly used at oil field exploration/production sites.

n. Gas - All natural gas, whether hydrocarbon or nonhydrocarbon or any combination or mixture thereof, including hydrocarbons, hydrogen sulfide, helium, carbon dioxide, nitrogen, hydrogen, casing-head gas, occluded natural gas from coal seams, compressed air and all other hydrocarbons not defined as "oil".

o. Location Site or Sites - The surface of a property in close proximity to production wells, production equipment, or the location of known releases of production scale or sludge containing NORM.

p. May - The word *may* is used to denote permission.

q. MEMA - Mississippi Emergency Management Agency Form RAD 5-2, Form RAD 5-3 and RAD 5-4.

r. Milliroentgen per hour (mR/hr) - A unit of gamma exposure rate. In the oil field, one mR/hr shall be equivalent to 1,000 microR per hour (μR/hr).

s. Millirem (mrem) - A unit of radiation dose. In the oil field, one mrem shall be equivalent to 1,000 microrem (μrem).

t. Mississippi Department of Health Regulations - Regulations for Control of Radiation in Mississippi, Part 801.

u. NORM - Technologically-enhanced naturally-occurring radioactive materials consisting, primarily, or ^{226}Ra (and daughter radiations) and ^{228}Ra (and daughter radiations) that are derived from the exploration and production activities of oil and gas operations within the territorial area of the State of Mississippi.

v. Oil - Crude petroleum oil and all other hydrocarbons which are produced at a well in liquid form by ordinary production methods and which are not the result of condensation of gas.

w. Operator - Any person who, duly authorized, is in charge of the development of a lease or the operation of a producing well.

x. Producer - An owner of drilling rights in property subject to this rule who has acquired its rights in said property for the purposes of developing, producing or otherwise utilizing the natural resources of oil and gas.

y. Property - Lands lying within an area recognized by the Oil and Gas Board as being within a "Field" as defined in Miss. Code. Ann. § 53-1-3(f).

z. Radiation Detection Instrument - A device, consisting of a detector and a ratemeter, that detects and records the characteristics of ionizing radiation.

aa. Radiation Surveyor - An individual who has training and experience in the following: Radioactivity measurements, monitoring techniques, and the use of instruments; conducting radiological surveys and evaluating results; evaluating exploration/production facilities for proper operations from a radiological safety standpoint; and familiarity with Board rules and regulations.

bb. Ratemeter - A read-out device that, when used with a detector forms a radiation detection instrument.

cc. Radioactive Material - Any solid, liquid or gaseous substance which emits radiation spontaneously.

dd. Radioactive Material Storage Area - An area where radioactive materials are stored or handled and where working conditions in the general area normally include consideration of radiological constituents as described in 29 CFR 1910.96 and Mississippi Department of Health Regulations.

ee. Release criterion (criteria) - A level of exposure rate or surface count rate, below which an item, device or property may be released for unrestricted use.

ff. Restricted Use - Equipment, components, materials, land areas (property), and other items that, by virtue of their levels of fixed and/or removable NORM are

maintained under the control of the operator or transferred to another producer for similar use.

gg. Rule 68 - Oil and Gas Board Statewide Rule 68, "Disposal of Naturally Occurring Radioactive Materials (NORM) Associated with the Exploration and Production of Oil and Gas".

hh. Shall - The word *shall* is to be understood as a requirement.

ii. Should - The word *should* is to be understood as a recommendation.

jj. Surface Disintegration Rate - An indication of the amount of radioactivity deposited on the surface of equipment. Surface disintegration rates are measured in units of "disintegrations per minute per 100 cm^2 area," with the window entrance of a Geiger counter radiation detector positioned approximately one (1) centimeter from the surface of interest. The surface disintegration rate is obtained by multiplying the count rate of the detector by the following correction factor:

$$CF = \frac{100}{(eff)\ Area},$$

where "eff" is the detector counting efficiency, determined from instrument calibration, and "Area" is the active area of the detector in units of "square centimeter."

kk. Survey - Evaluation of the radiological conditions at location sites incident to the production, use, release or presence of NORM.

ll. Total Effective Dose Equivalent (TEDE) - The sum of the deep dose equivalent (for external exposures) and the committed effective dose equivalent (for internal exposures). The TEDE is generally expressed in units of "millirem".

mm. Unrestricted Use - Equipment, components, materials, land areas (property), and other items that may be used, transferred, sold, or disposed of without regard for their radiological constituents.

3. Standard

a. Oil field exploration and production sites shall be operated and released in a fashion that ensures a TEDE of less than 100 millirem per calendar year due to exploration/production activities for workers and members of the general public.

b. Operations or operating site conditions that may cause workers or members of the general public to exceed 100 millirem TEDE in a calendar year due to exploration/production activities shall be controlled pursuant to Mississippi Department of Health regulations.

4. Surveys

a. Operators shall perform surveys of location sites, as necessary, to evaluate:

i. The magnitude of exposure rates in the vicinity of equipment;

ii. The magnitude of exposure rates above ground surfaces; and

iii. Radiological conditions in the event of non-routine circumstances including, but not limited to, equipment repairs, equipment maintenance, site maintenance, accidents and spills any of which result in release of production scales or sludges onto the surface.

b. All surveys shall be performed by a radiation surveyor.

c. Ground surface surveys shall be performed in accordance with generally accepted survey practices and, at a minimum, shall report the maximum readings for each 1 meter x 1 meter grid area over the well head, tank battery site, heater treater site, all surface pipe areas and other areas of the location site where contamination is likely to occur. Elsewhere on the location site, the maximum readings for each 10 meter x 10 meter grid area shall be reported.

d. All surveys shall be documented on Board Form No. 21 or on a form that contains equivalent information to Board Form No. 21.

e. Surveys shall be performed with a radiation detection instrument in accordance with the following requirements:

i. Radiation detection instruments shall be of sufficient sensitivity and accuracy to assess the radiation exposure rates from NORM found at exploration/production sites.

ii. Instruments shall be calibrated according to the guidelines of ANSI-N323 at least once every 12 months and following any repairs to the ratemeter and/or detector, with a radiation source traceable to the National Institute of Standards and Technology.

iii. The battery status and the response of the instrument to radiation from a check source shall be checked and recorded prior to the day's use.

f. If a survey documented on Board Form No. 21 (or equivalent) has not been performed at a location site, an initial survey shall be performed within one (1) year of the effective date of this Rule for wells permitted on or before the effective date of this Rule. For wells which are permitted after the effective date of this Rule, the initial survey shall be performed prior to the start of exploration/production operations and again two (2) years after the start of exploration/production operations.

g. After the initial survey of location sites, routine surveys shall be performed every five (5) years during exploration/production activities if the maximum exposure rate recorded in the last survey exceeds 50 microR per hour above background. Otherwise, they shall be performed every ten (10) years.

h. Surveys shall also be performed as necessary to evaluate radiological conditions in the event of non-routine circumstances as described in Section 4.a.iii. above.

5. Criteria for Site Operations

a. Personnel performing work at an exploration/production facility shall be trained in the hazards of the workplace pursuant to 29 CFR 1910.96(i).

b. Site access shall be controlled as follows:

i. Access to an exploration/production site with exposure rates in excess of 250 microR per hour above background in accessible locations shall be controlled by posting Caution Signs at the perimeter of the property which shall be visible from any and all accessible locations.

ii. Access to an exploration/production site with exposure rates in excess of 700 microR per hour above background in accessible locations shall be controlled by fencing the immediate area with a five foot high field fence or chain-link fence and by posting Caution Signs on the fence. The fence shall be located to restrict maximum exposure rates to 250 microR per hour above background.

iii. Access to an exploration/production site with exposure rates in excess of 5,000 microR per hour above background in accessible locations shall be controlled by fencing the immediate area with a five foot high field fence or chain-link fence, posting Caution Signs on the fence, and posting signs as required in 801.D.903(c) of the Mississippi Department of Health Regulations and 29 CFR 1910.96 at the location(s) where 5,000 microR per hour is exceeded.

iv. The limits contained in subsections (i) through (ii) are based on limited stay times. If it is anticipated that extended stay times might occur, the operator shall complete one of the following:

(1) Take actions to reduce the dose rate to which personnel are exposed (e.g., time, distance, shielding); or

(2) Establish a radiation protection program pursuant to Mississippi Department of Health regulations.

v. Operators shall be responsible for notifying all contractor personnel of the dose rates present at the facility(ies) where work will be performed. Once notified, the contractor shall be responsible for compliance with this rule.

vi. An operator may request an exception to the fencing requirements set forth above. Any such request shall be in writing to the Supervisor. Upon good cause shown, the Supervisor, in his or her discretion, may grant such an exception. Such written request and any response thereto shall be made a part of the applicable well file(s).

c. Site maintenance shall be controlled as follows:

i. Maintenance activities at sites with a maximum exposure rate of less than 50 microR per hour above background shall require no controls.

ii. Maintenance activities at sites with a maximum exposure rate in excess of 50 microR per hour above background shall require the prudent use of dust masks, or water sprays or other dust control methods as appropriate.

iii. Land maintenance and equipment maintenance/repair that may cause workers or contract personnel to exceed 100 millirem TEDE in a calendar year shall require control/licensing pursuant to Mississippi Department of Health Regulations.

6. Release of Property

a. Transfer to another producer.

i. Property may be transferred to another producer without regard for its radiological constituents.

ii. Copies of the most recent radiation survey documents shall be transmitted by the operator to the new producer prior to the property transfer.

b. Release for unrestricted use.

i. A production site may be released for unrestricted use after:

(1) All equipment contaminated to levels above the release criteria in 7.b.i. and 7.b.ii. has been removed from the property;

(2) A survey of the location site surface demonstrating that the property does not exhibit an exposure rate at any discrete point in excess of 50 microR per hour above background has been completed, documented, and furnished to the site owner; and

(3) A survey on the location site of exposure rates in at least five (5) boreholes per acre, with a minimum of three (3) boreholes per site, showing a maximum exposure rate less than 200 microR per hour including background. At least one (1) borehole shall be drilled at the location of the maximum surface exposure rate measurement. All boreholes shall be at least one meter deep, and shall be measured at 0.15 meter intervals.

ii. Land area remediation may be performed by the following methodologies in order to achieve the release criteria listed in 6.b.i.(2):

(1) No action;

(2) Excavating and transferring discrete areas of soil to a radioactive material storage area or for disposal under Rule 68; or

(3) Other remedial actions as approved, in advance, by the Board.

7. Criteria for Release of Equipment

a. Equipment may be transferred to another producer without regard for its radiological constituents.

b. Equipment that is released for unrestricted use shall:

i. Exhibit a surface disintegration rate on accessible internal and external surfaces of no greater than an equivalent of 2,000 dpm per 100 cm^2 above background; and

ii. Exhibit an exposure rate at a distance of 2.5 centimeters (1 inch) from the equipment surface of no greater than 25 microR per hour above background.

8. Records

a. The following records shall be maintained by the operator at the local operations office for the duration of operations at the site:

i. Site survey records;

ii. Instrument calibration records;

iii. Material transfer records; and

iv. Records setting forth the qualifications of the radiation surveyor.

b. The form of records may be paper copy or film copy of an original paper form.

c. Electronic records shall have an associated paper copy.

d. All such records shall be maintained by the operator for a minimum of ten (10) years after a property has been released for unrestricted use.

9. Exceptions

Except where otherwise stated, exceptions to any part of the above rule may be allowed upon good cause shown and upon proper Notice and Hearing of a petition filed with the Board requesting same.

10. Effective Date

This Statewide Rule (Rule 69), Board Order Number 73-96 shall take effect and be in force from and after June 1, 1996.

11. Validity

Should any section, subsection or other provision of this rule be declared by a court of competent jurisdiction to be invalid, that decision shall not affect the validity of the rule as a whole or any part thereof, other than the part so declared to be invalid, this Board hereby declaring that it would have adopted those partes of this rule which are valid and omitted any parts which may be invalid, if it had known that such part or parts were invalid at the time of the adoption of this rule.

[OGB Form 21 is attached to this Order as Exhibit "A" hereto and is incorporated herein for all purposes. It is hereby adopted.]

ORDERED AND ADJUDGED, this the 18th day of April, 1996.

MISSISSIPPI STATE OIL AND GAS BOARD

BY: Joseph D Jurcaro
CHAIRMAN

Thermodynamic Modeling of the Precipitation of Salts from Aqueous Solutions

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Abstract

Experimental database for the precipitation of chloride and sulfate salts from aqueous saline solutions by a miscible organic solvent was employed to test and evaluate a rigorous thermodynamic framework. The framework is derived from thermodynamic principles, which are based on the liquid-liquid equilibrium criteria, to predict the solubility phase behavior of the precipitation measurements. The precipitation measurements are modeled in terms of the solubilities of a given salt in the mother solvent (water), and in the mixed-solvents mixture (water and miscible organic solvent). The activity coefficients of the salt in the pure water and in the mixed-solvent mixture are expressed in terms of a power series function. The developed framework is reasonably adequate for predicting the solubility phase behavior of the precipitation measurements as well as for providing optimum interaction parameters.

INTRODUCTION

One goal of solution thermodynamics is to formulate models to describe quantitatively the phase behavior of pure fluids and mixtures. Most of these models are semi-empirical and their development and evaluation require phase equilibrium data and proper mathematical and statistical tools. Therefore, in engineering applications, one of the main advantages of thermodynamic models is the reduction of experimental efforts [1].

An important area of solution thermodynamics is the study of inorganics (electrolytes) phase equilibria. Knowledge of inorganics phase equilibria in pure and mixed solvents plays an important role in advancing chemical technologies (e.g., azeotropic and extractive distillations, saline water desalination, brine associated with oil production and geothermal energy production, precipitation and crystallization processes, partitioning processes in biochemical systems, etc.). A remarkably less amount of work in the field of inorganics thermodynamics, however, has been undertaken compared to organics thermodynamics [2]. This situation is attributed to the lack of [3]: (1) understanding of inorganics thermodynamics and aqueous chemistry (e.g., chemical and ionic identities), and thus the lack of developing rigorous theories; and (2) reliable data with which to formulate, test, and evaluate thermodynamic frameworks. Hence, the need for inorganic thermodynamics frameworks often justifies the efforts dedicated to the development of accurate correlation and prediction models.

Correlation and prediction of solubility phase behavior of inorganic species in organic-aqueous mixtures are of prime fundamental and practical importance in the precipitation process. This work is concerned with the formulation of thermodynamics frameworks as a means to predict phase behavior of the precipitation process. The impetus of

the modeling efforts in our work [4-9] was guided, in part, by three facts. First, the precipitation phenomena is a novel concept that does not appear in classical thermodynamics textbooks and requires attention. Second, predicting and understanding the thermodynamic phase behavior of salt solubilities in mixed-solvents mixtures provide an insight into the controlling factors influencing and characterizing the precipitation phenomena. Third, precipitation measurements are costly and time consuming; thus, it is important to have a model with a reliable prediction capability.

The objectives of this work were to: (1) develop a rigorous thermodynamics framework to model the solubility phase behavior of a given salt in a mixed-solvents mixture; and (2) employ an acquired precipitation database [3] to evaluate the viability of the developed framework equations in describing the phase behavior of the precipitation measurements, and in providing optimum interaction parameters for such measurements.

THERMODYNAMIC FRAMEWORK

The modeling effort was directed toward establishing semi-empirical expressions with a theoretical foundation for the precipitation measurements which would fulfill practical needs. A preference was given to model expressions which predicted mixture equilibrium properties by using pure component properties.

In the first part, thermodynamics principles of liquid-liquid equlibliria were used to express the salt solubility in a mixed-solvents mixture. In the second part, a power series function was employed to express the activity coefficient expressions. The precipitation measurements and the model's equations were related in the third part. Following is a presentation of the developed framework equations.

Salt Solubility in a Mixed-Solvents Mixture

Precipitation measurements were modeled in terms of salt solubility in the reference solvent (water), whereby total volume does not change during the precipitation process, and the salt solubility in both solvent (water and miscible organic solvent). The change in Gibbs free energy for the transformation of a dissolved salt in a liquid solution containing pure water (α) to a solution with less salt solubility containing both water and miscible organic solvent (β) can be expressed as follows [10]:

$$dG = \mu_i^{L\alpha} - \mu_i^{L\beta} = RT\left[\ln \frac{\hat{f}_i^{L\alpha}}{\hat{f}_i^{L\beta}}\right] \quad (1)$$

or

$$\hat{f}_i^{L\alpha} = \hat{f}_i^{L\beta} \quad (2)$$

where $\mu_i^{L\alpha}$ is the chemical potential of a dissolved salt in pure water, $\mu_i^{L\beta}$ is the chemical potential of a dissolved salt in a liquid mixture (water and organic), R is the gas constant, T is the temperature, $\hat{f}_i^{L\alpha}$ is the fugacity of a dissolved salt in pure water, and $\hat{f}_i^{L\beta}$ is the fugacity of a dissolved salt in a liquid mixture (water and organic). Equation (1) indicates that the fugacity of a dissolved salt in pure water is equal to its fugacity in a liquid mixture containing both water and miscible organic solvent. However, the fugacity of a given solute in a liquid mixture can be expressed as follows [10]:

$$\hat{f}_i^{L} = x_i \gamma_i f_i^{\circ} \quad (3)$$

where X_i is the mole fraction of a solute, γ_i is the symmetric activity coefficient of a solute, and f_i^o is the fugacity of the hypothetical pure liquid. As such, Equation (2) can be rewritten as follows:

$$\gamma_i^{\alpha} x_i^{\alpha} = \gamma_i^{\beta} x_i^{\beta} \tag{4}$$

If the salt is labeled as species 1, water as species 2, and miscible organic solvent as species 3, Equation (4) can be expressed as follows:

$$\gamma_{1,2} x_{1,2} = \gamma_{1,m} x_{1,m} \tag{5}$$

or

$$\ln\left[\frac{\gamma_{1,m}}{\gamma_{1,2}}\right] = \ln\left[\frac{x_{1,2}}{x_{1,m}}\right] \tag{6}$$

where $\gamma_{1,m}$ is the activity coefficient of a given salt in the mixture (water and organic), $\gamma_{1,2}$ is the activity coefficient of a given salt in pure water, $x_{1,2}$ is the solubility of a salt in pure water, and $x_{1,m}$ is the solubility of salt in the mixture.

Activity Coefficients Expressions Based on The Power Series Function

The activity coefficient of a given salt in pure water or in a mixture containing both water and organic solvent at constant temperature and pressure can be related empirically as a power series function to the compositions of both salt and organic solvent [11]. Water is assumed to be a structureless dielectric continuum and all deviations from ideality are due to electrostatic interaction [12]. As

such, activity coefficients of a given salt in pure water and in a mixture containing both water and miscible organic solvent as follows:

$$\ln \gamma_{1,m} = \sum_{y,z}^{\infty} \Lambda_{yz} x_{1,2}^{z} x_{3}^{y} \qquad (7)$$

where y and z are integer powers, Λ_{yz} represents interaction parameters, and x_3 is the salt-free organic mole fraction. Expanding Equation (7) for $y + z \leq 3$, leads to the following expression for the activity coefficient of a given salt in a mixture of water and miscible organic solvent:

$$\ln \gamma_{1,m} = \Lambda_{00} + \Lambda_{01} x_{1,2} + \Lambda_{10} x_3 + \Lambda_{11} x_{1,2} x_3 + \Lambda_{02} x_{1,2}^2 + \Lambda_{20} x_3^2 + \Lambda_{03} x_{1,2}^3 + \Lambda_{12} x_{1,2}^2 x_3 + \Lambda_{21} x_{1,2} x_3^2 + \Lambda_{30} x_3^3 \qquad (8)$$

Similarly, an expression for the activity coefficient of a given salt in pure water ($x_3 = 0$) can be generated as follows:

$$\ln \gamma_{1,2} = \Lambda_{00} + \Lambda_{01} x_{1,2} + \Lambda_{02} x_{1,2}^2 + \Lambda_{03} x_{1,2}^3 \qquad (9)$$

Therefore, Equation (6) can be expressed as follows:

$$\ln\left[\frac{\gamma_{1,m}}{\gamma_{1,2}}\right] = \ln\left[\frac{x_{1,2}}{x_{1,m}}\right] = \Lambda_{10} x_3 + \Lambda_{11} x_{1,2} x_3 + \Lambda_{20} x_3^2 + \Lambda_{12} x_{1,2}^2 x_3 + \Lambda_{21} x_{1,2} x_3^2 + \Lambda_{30} x_3^3 \qquad (10)$$

If Equation (7) expanded with respect to $y + z \leq 2$, Equation (10) would be reduced to the following form:

$$\ln\left[\frac{\gamma_{1,m}}{\gamma_{1,2}}\right] = \ln\left[\frac{x_{1,2}}{x_{1,m}}\right] = \Lambda_{10}x_3 + \Lambda_{11}x_{1,2}x_3 + \Lambda_{20}x_3^2 \qquad (11)$$

If $\mathbf{y} + \mathbf{z} \leq \mathbf{1}$ is used in expanding Equation (7), Equation (10) would be collapsed to the following form:

$$\ln\left[\frac{\gamma_{1,m}}{\gamma_{1,2}}\right] = \ln\left[\frac{x_{1,2}}{x_{1,m}}\right] = \Lambda_{10}x_3 \qquad (12)$$

The form of Equation (12) is similar to the well-known Setschenow's equation [13].

As the precipitation of a given salt increases with the increase in the amount of miscible organic solvent, the solubility of such a salt decreases ($x_{12} \rightarrow 0$). Thus, for high precipitation fractions of a given salt, Equation (10) can be reduced to the following form:

$$\ln\left[\frac{x_{1,2}}{x_{1,m}}\right] = \Lambda_{10}x_3 + \Lambda_{20}x_3^2 + \Lambda_{30}x_3^3 \qquad (13)$$

Similarly, Equation (11) can be reduced as follows:

$$\ln\left[\frac{x_{1,2}}{x_{1,m}}\right] = \Lambda_{10}x_3 + \Lambda_{20}x_3^2 \qquad (14)$$

Relation between Model's Equations and Precipitation Measurements

Experimentally, precipitation measurements are given in terms of the salts precipitation fractions (P) upon the addition of a miscible

organic solvent. Therefore, the left-hand side of Equations (6) and (13) can be related to the salt precipitation fraction as follows [3]:

$$\ln\left[\frac{x_{i,m}}{x_{1,2}}\right] = -\ln[1 - P] \tag{15}$$

The solvent compositions are typically described by their volume fractions [6,14]. Hence, water and organic mole fractions (x_2 and x_3) can be expressed in terms of their salt-free volume fractions ($\theta_2 + \theta_3 = 1$) as given in the following relation:

$$\theta_i = \left[\frac{x_i v_i}{\sum_{i=2}^{3} x_i v_i}\right] \tag{16}$$

where v_i is the pure solvent molar volume. It should be pointed out that the right-hand side of Equation (15) is always negative, therefore Equations (11) and (13) can be rewritten as follows:

$$\ln[1 - P] = \Lambda_{10}\theta_3 + \Lambda_{20}\theta_3^2 + \Lambda_{30}\theta_3^3 \tag{17}$$

and

$$\ln[1 - P] = \Lambda_{10}\theta_3 + \Lambda_{20}\theta_3^2 \tag{18}$$

RESULTS AND DISCUSSIONS

Database Used

Precipitation database for systems including monovalent and divalent cations in forms of chloride, and sulfate salts using isopropylamine as a precipitation agent previously acquired were employed. However, selected systems were used to demonstrate the viability of the developed framework equations. Detailed information for such database can be found elsewhere [3].

Data Reduction Procedure

Regressions of the precipitation measurements were performed using the weighted least squares objective function (SS). A Marquardt nonlinear regression procedure was employed in the precipitation calculations [15]. The objective function, SS, used for the evaluation of the model equations is given as follows:

$$SS = \sum_{i=1}^{NP} \left[\frac{Y_{Cal} - Y_{exp}}{Y_{exp}} \right] \tag{19}$$

where Y_{cal} is the calculated variable, and Y_{exp} is the experimental variable, and given as follows:

$$\mathbf{Y = \ln[1 - P]} \tag{20}$$

According to Equation (19), the root-mean-square-error (RMSE) provides an appropriate measure for overall performance of the model for a given data set more so than %AAD.

Model Evaluation

Detailed information for the tested systems (magnesium chloride and magnesium sulfate) containing the volume fraction of isopropylamine (θ_3), the solvents volume ratio (V_R), the experimental precipitation fractions (%P) along with their uncertainties (σ_p), and the predicted precipitation fractions by both Equations (17) and (18) are presented in Tables 1 and 2.

The 3-Power equation, Equation (17), contain three interaction parameters, while the 2-Power equation, Equation (18), contain two interaction parameters. For the tested systems, Equation (18), with two interaction parameters, provides an adequate representation. However, significant improvements were achieved when Equation (17), with three interaction parameters, was used (for magnesium chloride system at 5,000 mg/L; Equation (18): RMSE = 0.0479, %AAD = 6.65; Equation (17): RMSE = 0.0129, %AAD = 2.07; for magnesium sulfate system at 1,000 mg/L; Equation (18): RMSE = 0.0289, %AAD = 6.47; Equation (17): RMSE = 0.0264, %AAD = 4.18). Such improvements were attributed to the unsymmetric form of Equation (17) with respect to θ_3. Figures 1 and 2 illustrate the prediction abilities of Equations (17) and (18) in representing the tested systems. These figures show plots of the left-hand side of Equations (17) and (18), ln[1-P], versus θ_3.

Comparisons of the experimental precipitation fractions (%P) at different solvents volume ratio (V_R) along with their uncertainties and the predicted precipitation fractions by the optimum predictive equation, Equation (17), are presented in Tables 1 and 2, and shown in Figures 3 and 4. Such comparisons indicate that the precipitation fractions are predicted accurately by Equation (17), the optimum

predictive equation. The produced optimum interaction parameters, however, can be used to estimate the precipitation fractions of the studied systems at a higher solvents volume ratio where no experimental data are available (e.g., V_R = 3.0 or 4.0, etc.). This would provide economy of experimental effort, and cost savings (not to waste the organic solvent).

CONCLUSIONS

A rigorous framework derived from thermodynamic principles of liquid-liquid equilibrium criteria was developed to correlate and predict the precipitation measurements. The activity coefficient of a given salt in a mixed-solvent mixture was related to the activity coefficient of such a salt in the reference solvent (water). The power series function was employed to express the activity coefficients. Two model equations were provided by the framework; the 2-Power equation with two interaction parameters (Equation (17)), and the 3-Power equation with three interaction parameters (Equation (18)).

The tested systems were adequately predicted by the two interaction parameters equations; Equation (18). However, Equation (17), with three interaction parameters, were more accurate in representing the precipitation measurements than Equation (19). Optimum interaction parameters were provided by the model equations. Such parameters can be used as predictive tools to estimate the precipitation fractions for tested systems for which no experimental data are available.

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Table 1

Experimental and predicted precipitation fractions for magnesium chloride at 5,000 mg/L

θ_3	V_R	%P/ σ_p	%P ± σ_p	Predicted %P	
				Eq. (18)	Eq. (17)
----------Precipitation Measurements----------					
0.091	0.1	18.2	20.1	12.7	17.0
		1.9	16.3		
0.167	0.2	21.4	23.2	19.1	21.5
		1.8	19.6		
0.286	0.4	30.1	31.8	29.9	29.7
		1.7	28.5		
0.375	0.6	33.6	35.2	36.7	34.8
		1.6	32.1		
0.444	0.8	40.4	41.9	41.3	39.1
		1.5	38.9		
0.500	1.0	43.0	44.4	44.7	42.9
		1.4	41.6		
0.583	1.4	48.9	50.2	49.3	49.7
		1.3	47.6		
0.667	2.0	58.1	59.2	53.3	57.8
		1.1	57.0		

----------Model Evaluations----------

Equation (17): %AAD=2.07; RMSE=0.0129
Λ_{10}=1.9523; Λ_{20}=-3.6732; Λ_{30}=4.0251

Equation (18): %AAD=6.65; RMSE=0.0479
Λ_{10}=1.3157; Λ_{20}=-0.2596

%AAD: Percent Average Absolute Deviation; RMSE: Root Mean Square Error.

Table 2

Experimental and predicted precipitation fractions for magnesium sulfate at 1,000 mg/L

θ_3	V_R	%P/ σ_P	%P ± σ_P	Predicted %P	
				Eq. (18)	Eq. (17)
----------Precipitation Measurements----------					
0.091	0.1	15.3 1.4E00	16.7 13.9	10.4	14.0
0.167	0.2	18.1 1.4E00	19.5 16.7	16.0	17.5
0.286	0.4	25.7 1.3E00	26.9 24.4	27.1	26.7
0.375	0.6	32.4 1.2E00	33.5 31.2	35.1	33.6
0.444	0.8	39.9 1.0E00	40.9 38.8	41.0	39.4
0.500	1.0	47.0 9.3E-1	47.9 46.0	45.5	44.4
0.583	1.4	53.3 8.3E-1	54.1 52.4	52.0	52.5
0.667	2.0	59.5 7.6E-1	60.3 58.8	58.0	61.1
----------Model Evaluations----------					
Equation (17):		%AAD=4.18; RMSE=0.0264 Λ_{10}=1.3745; Λ_{20}=-1.8036; Λ_{30}=2.7991			
Equation (18):		%AAD=6.47; RMSE=0.0289 Λ_{10}=0.9610; Λ_{20}=0.5091			

%AAD: Percent Average Absolute Deviation; RMSE: Root Mean Square Error.

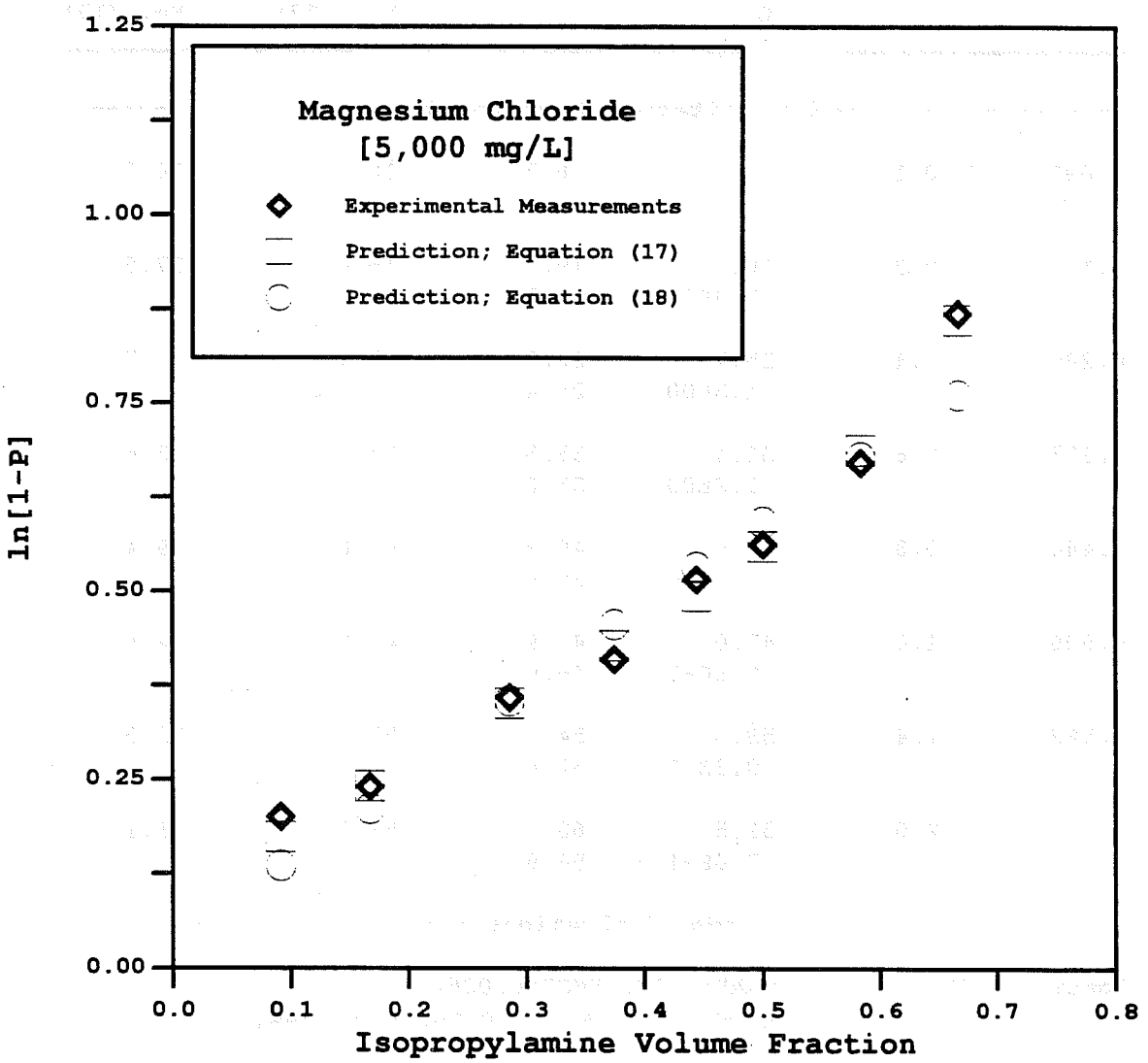


Figure 1. Precipitation of 5,000 mg/L Chloride Ion from Magnesium Chloride System

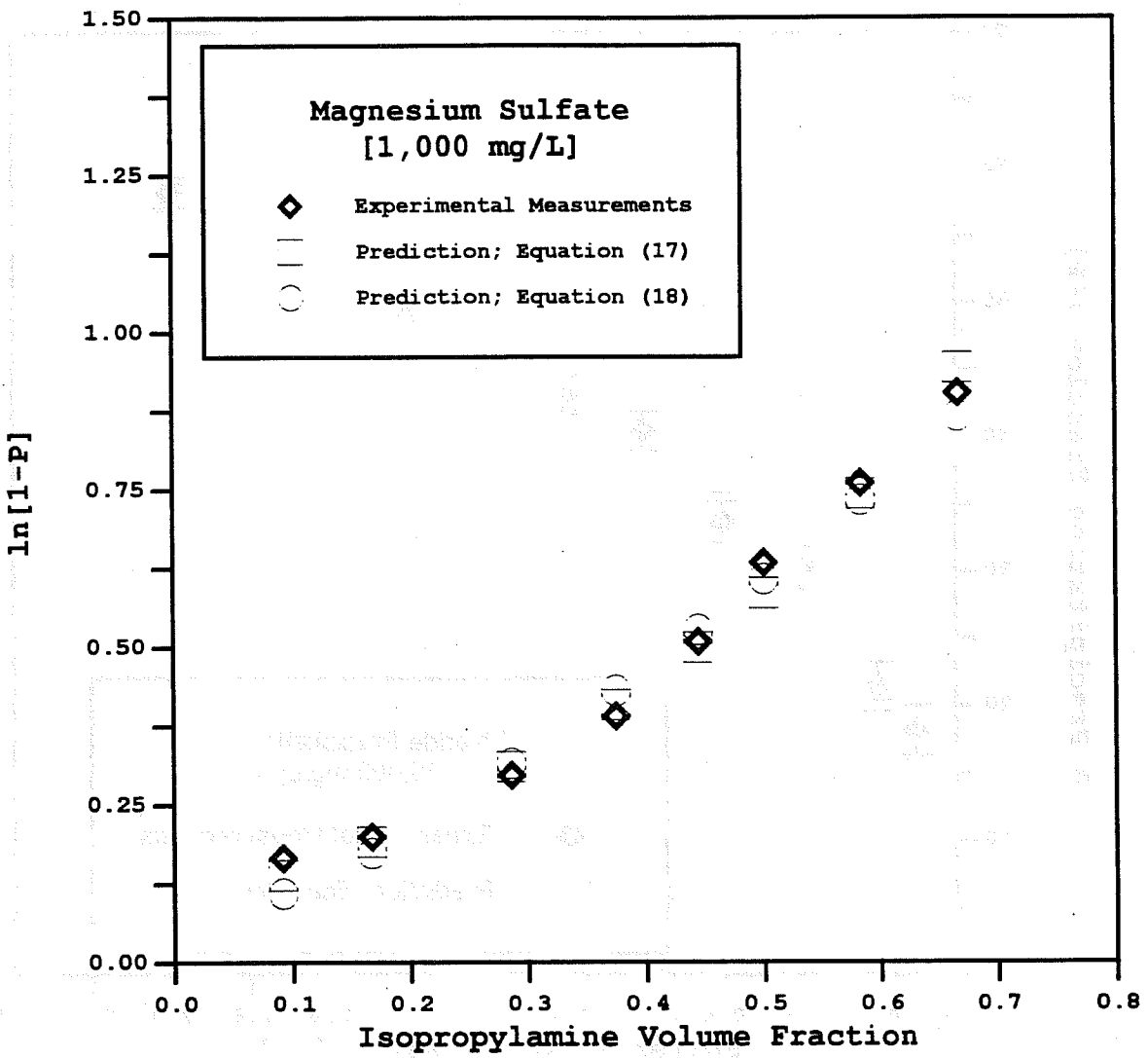


Figure 2. Precipitation of 1,000 mg/L Sulfate Ion from Magnesium Sulfate System

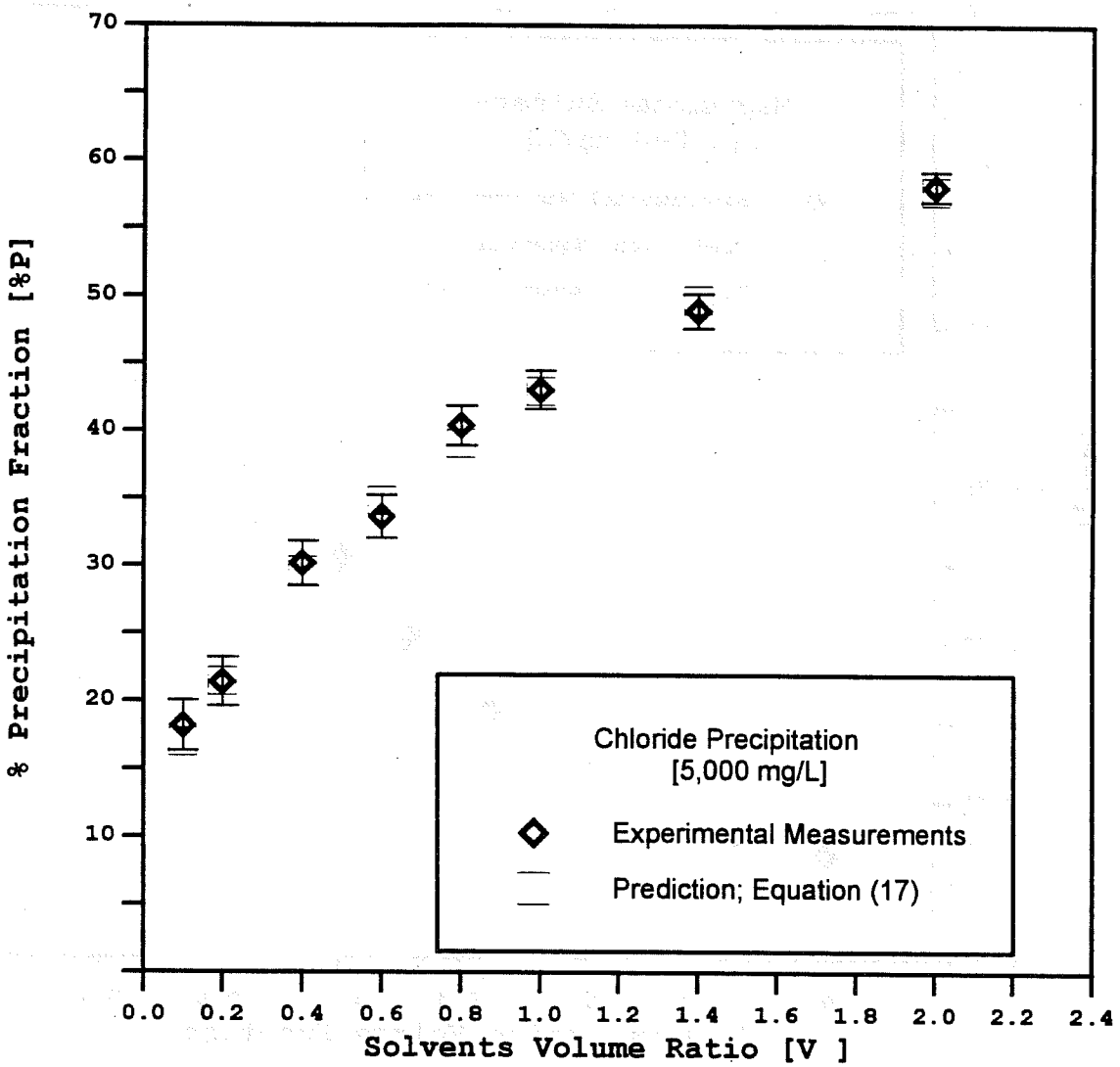


Figure 3. Precipitation Fraction for Magnesium Chloride System at 5,000 mg/L

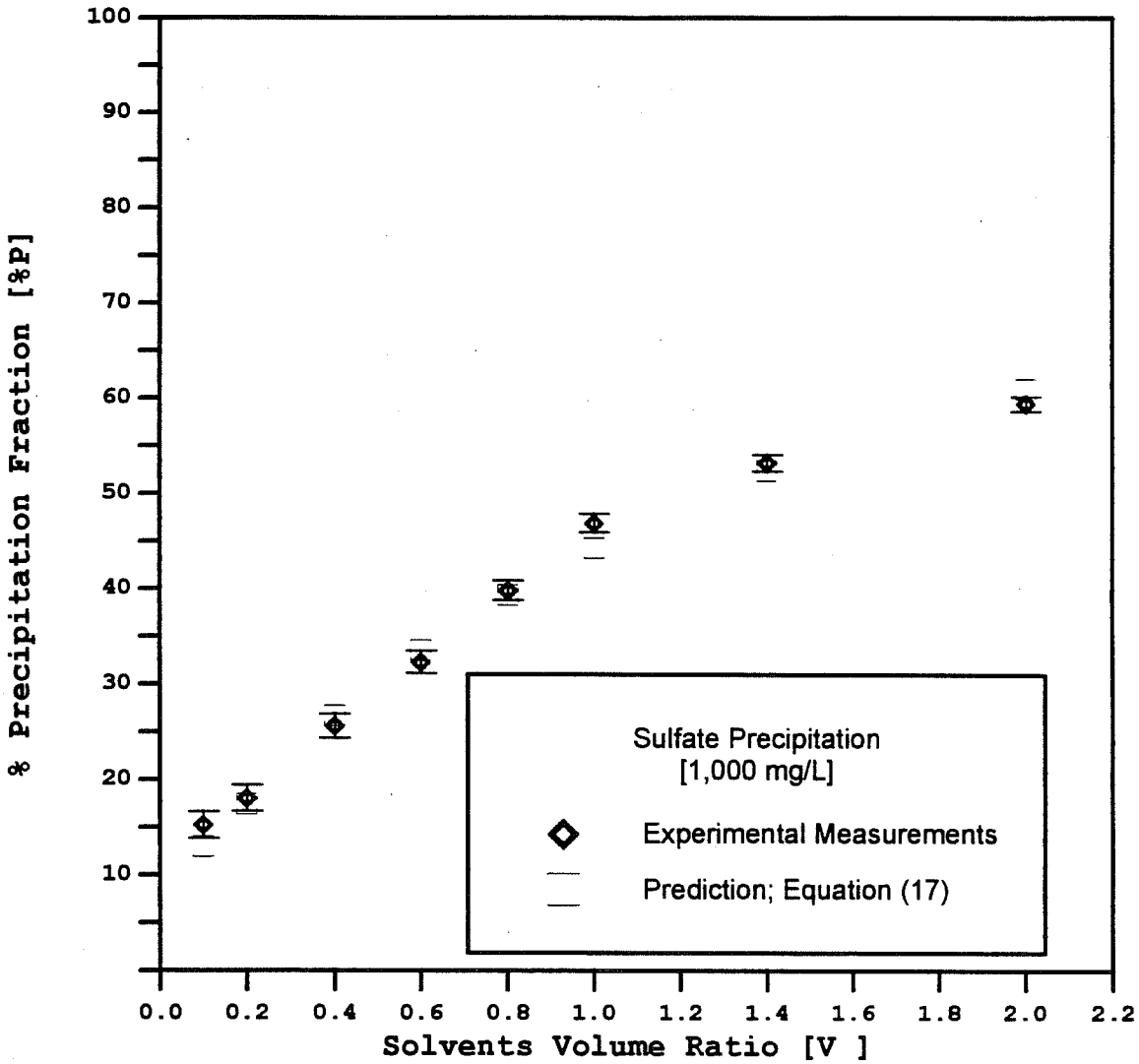
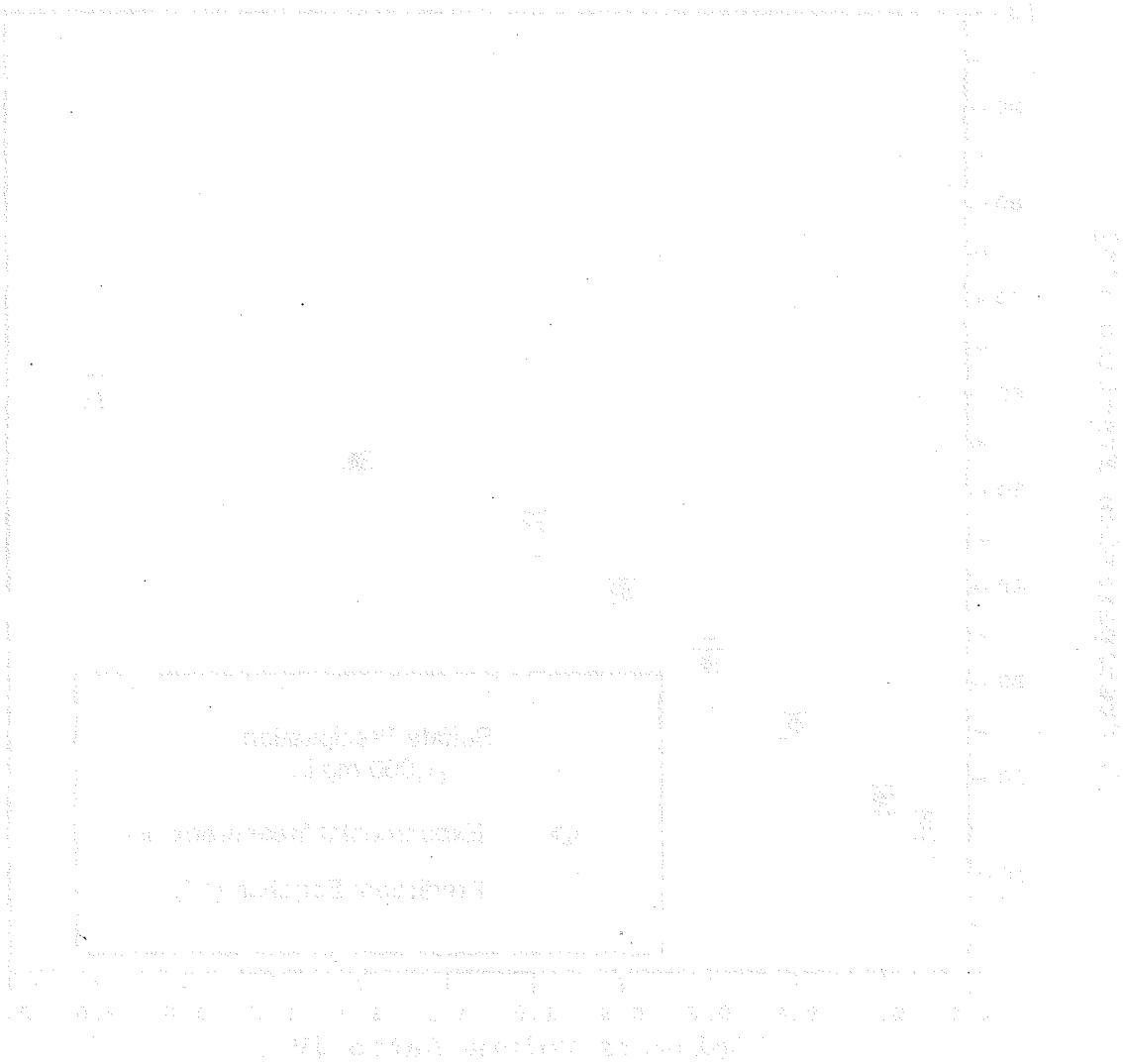


Figure 4. Precipitation Fraction for Magnesium Sulfate System at 1,000 mg/L



Anomalous ^{226}Ra in Pore Fluids from Barite Chimney Area on the Gulf of Mexico Continental Slope

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Abstract

The radium concentration of pore fluids from sites where active barite deposition occurs on the Gulf of Mexico Continental slope range from 8,680 to 256,857 dpm/100 liters. These concentrations are consistent with the range of radium values measured in produced waters from offshore platforms. A strong positive correlation has been determined to exist between pore fluid salinity and radium activity. The radium concentrations of these pore fluids are highly anomalous since they exceed by a factor of 658 to 19,500 the values reported from the Gulf of Mexico deep water (13.2 dpm/100L). Therefore, a new radium contributor to the Gulf of Mexico is proposed. This study indicates that the environmental impact of the natural discharge of the highly radioactive fluids on the Gulf of Mexico sea floor and habitats needs to be investigated.

Introduction

Investigations into the occurrence of radium in the Gulf of Mexico indicated that the Ra concentrations in bottom and surface water are higher than those in the Caribbean Sea (Reid, 1979, 1984; Key, 1981). Therefore, a measurable internal radium source was proposed to exist in the Gulf of Mexico. This radium source was attributed either to the northern shelf (i.e., Reid, 1984), or to the longer residence time of the water in the Gulf of Mexico (i.e., Key, 1981).

Submersible dives undertaken with the Johnson-Sea-Link (dive 3559 and 3566) on the Gulf of Mexico slope offshore Louisiana (Garden Banks Block 382, 27° 37.77′ N; 92° 28.08′ W, and Mississippi Canyon Block 929, 28° 01.46′ N; 89° 43.63′ W. Figure 1) in July of 1993 led to the discovery of barite chimneys occurring on the seabed in association with hydrocarbon-rich fluid venting features consisting principally of active mud volcanos (Fu et al., 1994).

In this paper ^{226}Ra measurements of the pore fluids sampled from the chimney areas are present. It is shown that these pore fluids are anomalously enriched in ^{226}Ra. A new radium source to the Gulf of Mexico is proposed. This may be useful for the environmental impact assessments in this region.

Methods

Piston cores collected by the submersible (at Garden Banks Block 382, and at Mississippi Canon Block 929) were brought into the laboratory aboard the Johnson-Sea-Link, where pore

fluids were squeezed using the method developed by Jahnke (1988). The pore fluids passed into a plastic disposable syringe inserted into the core at 3-4 cm depth intervals. The fluids were filtered through a 0.20 μm filter capping the syringe, acidified with HNO_3 to pH <2, and stored in 15 ml size glass bottles permanently sealed with rubber stoppers and aluminum vacuum caps.

Analyses for ^{226}Ra were conducted with modifications of liquid scintillation techniques (Prichard et al., 1980). A 10 ml of toluene was first transferred to a 20 ml liquid scintillation vial, and then about 5 ml of pore fluids was ejected to the bottom of the vial using a plastic syringe. The vial was sealed and stored for at least three weeks prior to analysis. The Rn content resulting from alpha decay of ^{226}Ra was then assayed using a liquid scintillation counter. The specific activity of ^{226}Ra in the sample is calculated from the counting data, and detection efficiency which was determined by measuring the ^{226}Ra blanks and standards. Based on multiple analyses of standards, the average uncertainties (1σ as %) in the radium values is 4.6%. In addition, pore water salinity was determined by a Goldberg Refractometer on the ship.

Results

The activity ^{226}Ra and salinity of ten pore fluids analyzed in this study are shown in table 1. The salinity range from 45 to 139 ppt, while the ^{226}Ra activity range from 8680 to 256857 dpm/100L. As shown in Fig. 2, a significant relationship exists between salinity and ^{226}Ra activity with a correlation coefficient (r) of 0.96.

One pore fluids depth profiles for ^{226}Ra activity and salinity from Garden Banks Block 382 were shown in Fig. 3. The salinity and ^{226}Ra activity show a maxima at 13 and 16 cm respectively and then decrease.

Discussion and Conclusions

Previous studies indicated that there is a measurable internal radium source in the Gulf of Mexico (Reid, 1979, 1984; Key 1981), but involvement of the source(s) has not been demonstrated. For example, Key (1981) found the average near-bottom radium for the Gulf of Mexico (13.2 dpm/100L) is higher than the Caribbean Sea (12.3 dpm/100L), and her suggested that the most likely reason is the residence time of water in the Gulf of Mexico is much longer for sedimentary flux to be the source.

The study conducted by Reid (1979) indicated that: (1) the top 100 m of the central Gulf of Mexico has a greater mean specific activity of ^{226}Ra by 1.1 dpm/100 kg than the Caribbean Sea; and (2) the increase of ^{226}Ra activity with depth is grater in the Gulf of Mexico than that in Caribbean Sea. He attributed the excess of ^{226}Ra in the Gulf of Mexico (compared to the Caribbean Sea) to either the deep (about 600 m) injection of radium produced after the water flowed out of the Caribbean Sea, or the longer residence time for water in the subsurface western Gulf of Mexico to allow greater accumulation of radium being removed from the surface layer by biological processes.

In another study, Reid (1984) also found a significant increase of ^{226}Ra activity from 1973

to 1976 in the upper 100 m of the Gulf of Mexico, and he attributed the excess source radium to the northern shelf of the Gulf of Mexico.

Cores of this study were sampled on the Gulf of Mexico Continental slope at 560-700 m water depth where active barite deposits occurs, and where hydrocarbon-rich fluid venting is pervasive (Fu et al. 1994). Thus, the pore fluids squeezed from the cores should represent the mixture o of the venting fluids and sea water. The average concentration of ^{226}Ra in the bottom water of the Gulf of Mexico is 13.2 dpm/100L (Key, 1981). In contrast, the ^{226}Ra of pore fluids in the study range from 8680 to 256857 dpm/100, about a factor of 658 to 19500 higher over that of bottom water. This suggests that the Ra in the pore fluids and the venting fluids can freely diffuse into bottom water and water column of the Gulf of Mexico.

The impact of the excess radium of the venting fluids on the Gulf of Mexico water column is not known presently but the gullies filled with highly radioactive fine barite sediment and the occurrence of radium-rich barite chimneys (Fu, unpublished data) over extensive areas suggest that the phenomena is widespread on the sea floor. Thus, these Ra-rich venting fluids on the sea floor may be one of the major controlling factors to the higher Ra found previously in both bottom and surface water in the Gulf of Mexico. In addition, the venting are not part of a continuum, but function periodically and with varied intensities because fault-related venting are not continually active (Roberts et al., 1990), this periodical venting event may **have** contributed to the temporal variability of ^{226}Ra in the near-surface Gulf of Mexico found by Reid (1984). Therefore, the environmental impact of the natural discharge of the highly radioactive fluids on the Gulf of Mexico sea floor needs to be investigated.

High radium concentrations have been found in different kinds of formation waters and the origin of the radium is still debatable (i.e., Kraemer and Reid 1984; Kronfeld et al., 1991,1992). The presence of a shallow salt diapir under the sample area, identified by high-resolution data (Shell Oil Company), the direct observation of gaseous hydrocarbon and fluid venting during sampling, and the similar salinity-Ra relationship to the one exists for the produced waters from offshore platform (Figure 4) made us to speculate that the high radium levels in the fluids advecting to the sea floor originate from leaching of salt dome and sheets, deep-seated, kerogen-rich, source rocks by highly saline formation fluids.

Elemental chemistry coupled with isotopic (i.e., strontium) analyses of the venting fluids, now in progress, are likely to lead to a better understanding of a number of questions that remain unanswered at present.

Acknowledgements

We thank the captain and the crew of R/V Seward Johnson and the pilots of the Johnson-Sea-Link submersible for their assistance with sampling. Submersible dives in 1993 were supported by funds from NOAA National Undersea Research Center, University of North Carolina at Wilmington. The research is supported in part by Grants from Shell Oil Company, Grants-in-Aid from the Gulf Coast Association of Geological Societies, Geological Society of America, and Sigma-Xi Society.

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Table 1. ^{226}Ra and salinity of pore fluids from barite chimney area on the Gulf of Mexico Continental slope.

Figure 1. Map showing the study area on the continental slope of the Gulf of Mexico.

Figure 2. ^{226}Ra-salinity relationship in pore fluids from barite chimney area on the Gulf of Mexico Continental slope.

Figure 3. Pore fluids depth profiles for ^{226}Ra activity and salinity from the core 3566-Pw-1 at Garden Banks Block 382.

Figure 4. ^{226}Ra-salinity relationship in formation waters. Solid triangle represent the data of this study, Open circles represent data published by Kraemer and Reid (1984), and Rabalais et al. (1991).

Table 1.

Sample name	Depth (cm)	Salinity (o/oo)	Ra-226 (dpm/100L)
Mississippi Canyon Block 929			
3562-Pw-1, 20	6	64	10134
3559-Pw-2, 14	4	80	17947
3559-Pw-2, 32	22	110	68249
Garden Banks Block 382			
3566-Pw-1, 15	7	134	157293
3566-Pw-1, 18	10	127	126107
3566-Pw-1, 21	13	139	225564
3566-Pw-1, 24	16	135	256857
3566-Pw-1, 27	19	127	119978
3566-Pw-1, 30	22	119	64434
3566-Pw-2, 30	4	45	8680

Figure 1.

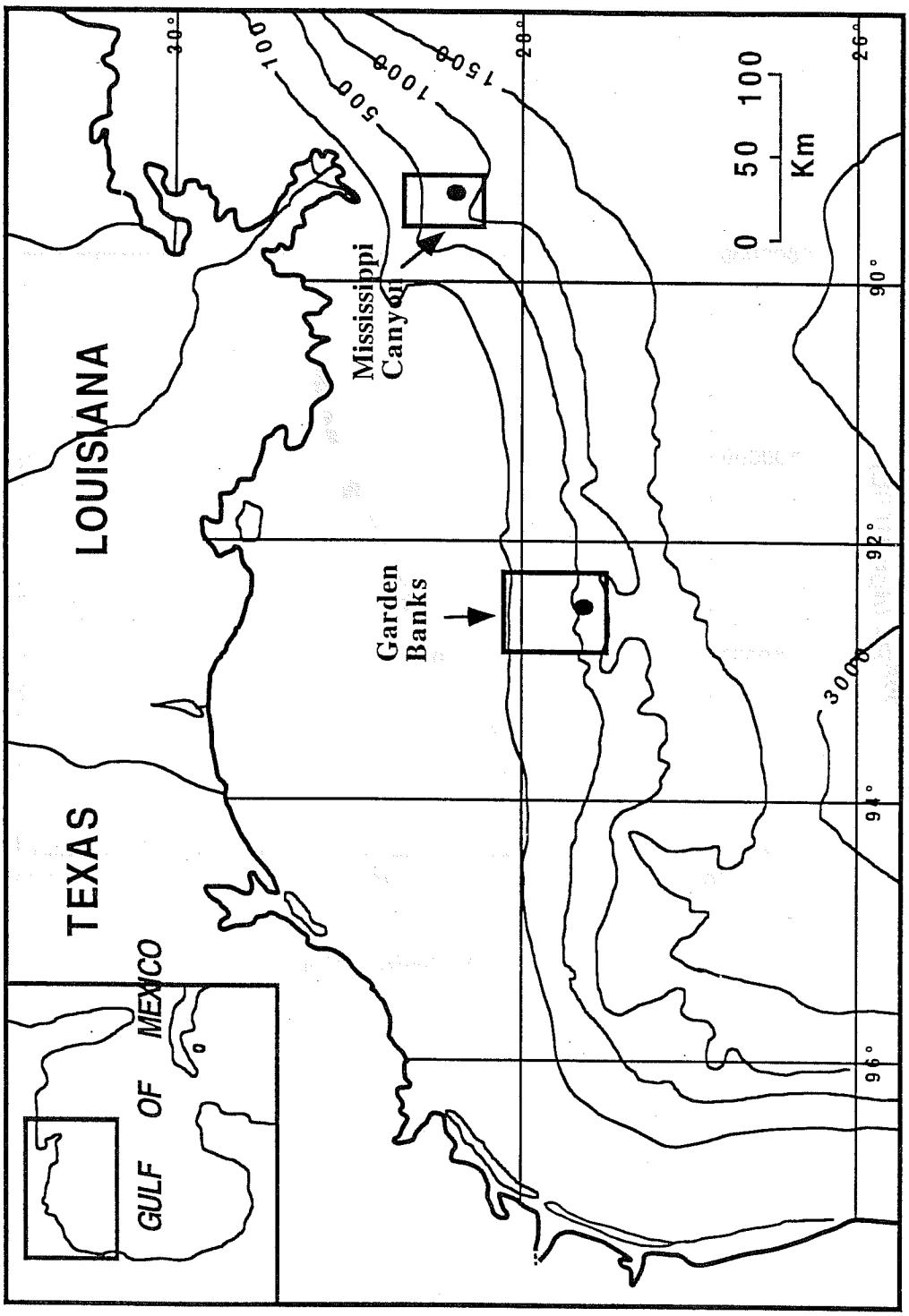

LOUISIANA
TEXAS
GULF OF MEXICO
Mississippi Canyon
Garden Banks
0 50 100
Km
100
500
1000
1500
2000
3000
30°
28°
26°
96°
94°
92°
90°

Figure 2.

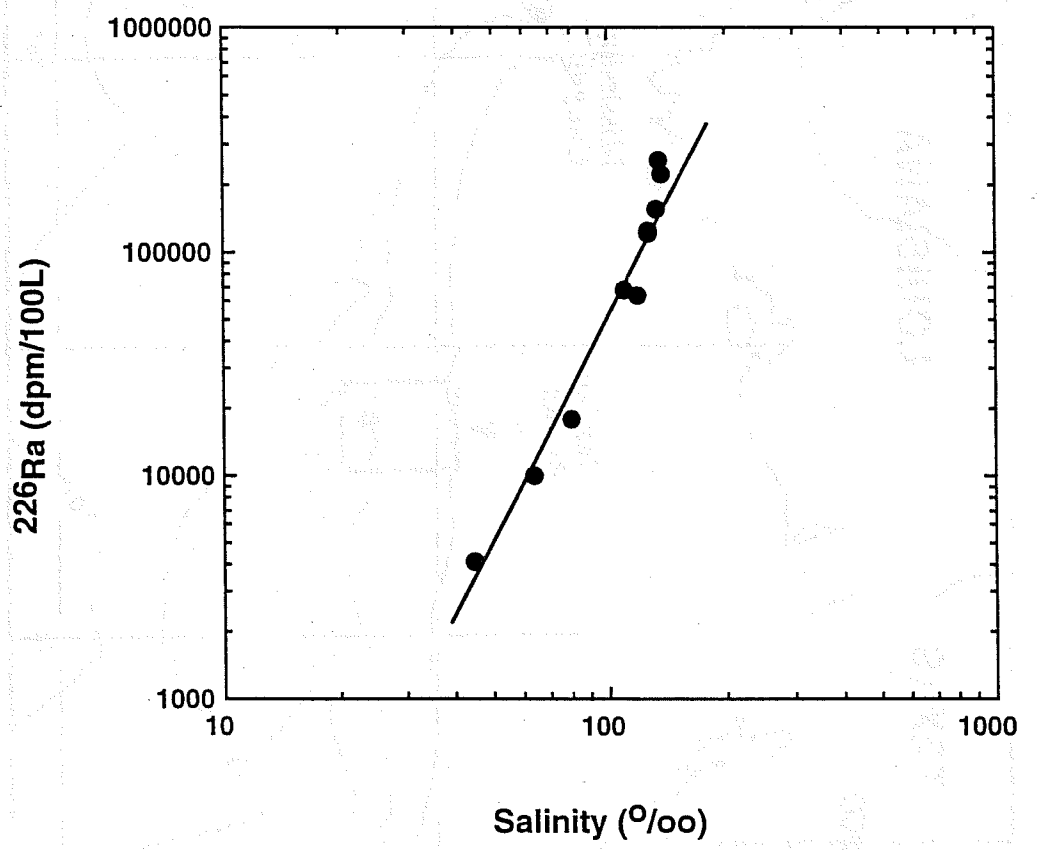

1000000
100000
10000
1000
10
100
1000
226Ra (dpm/100L)
Salinity (o/oo)

Figure 3.

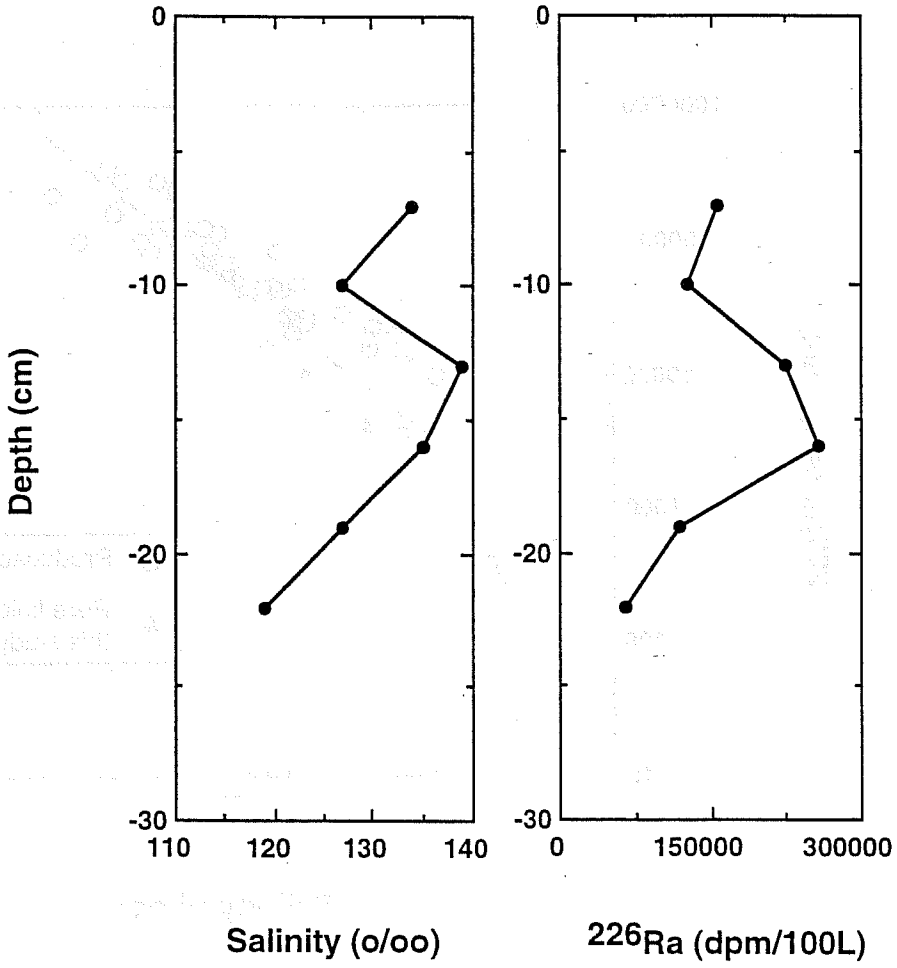
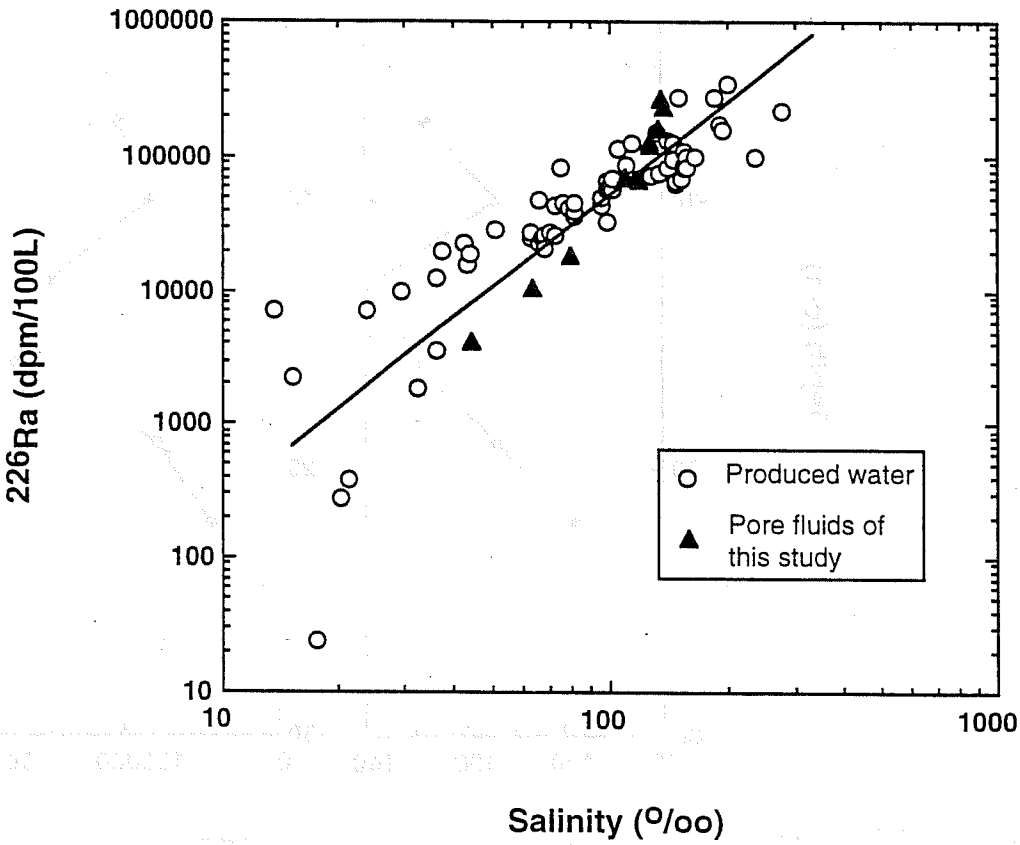

0
-10
-20
-30
Depth (cm)
110
120
130
140
Salinity (o/oo)
0
150000
300000
226Ra (dpm/100L)

Figure 4.


1000000
100000
10000
1000
100
10
10
100
1000
226Ra (dpm/100L)
Salinity (o/oo)
Produced water
Pore fluids of this study

Results from Bench-Scale Testing of a Mobile NORM Treatment and Disposal System.

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Abstract

A mobile NORM treatment and disposal system is currently under development by BPF, Inc. This system is comprised of three trailer-mounted processing modules which can process and dispose of a variety of NORM wastes typically generated during oil and gas production operations. The three treatment modules are the sorting/assay module, the solvent extraction module and the thermal pre-treatment module. The sorting/assay module is used to perform volume reduction on the NORM waste as well as a 100% radioassay on the residual cleaned solids. Based on measured radioactivity determined via gamma spectroscopy, soil/sludge/scale is separated according to user-defined thresholds determined by the regulatory limits for the Ra-226 and/or Ra-228 content. The solvent extraction module allows for the chemical dissolution of various NORM solids including acid and water soluble species. Relatively insoluble barium sulfate is dissolved using a proprietary barium sulfate dissolver. The thermal pre-treatment module can be used as the primary de-oiling step. Clean residual solids are returned to the lease holder for disposal following a 100% radioassay to verify that they have radioactivity below regulatory limits. The process solutions are disposed of by injection into salt-water disposal or injection wells as either a slug or via slipstreaming. Results from the laboratory tests used to define the process chemistry are presented along with the initial bench-scale field trial results including the reduction of radioactivity achieved in the residual solids. This work is supported by the Department of Energy under Contract No. DE-FC21-95MT30081.

Introduction

Naturally Occurring Radioactive Materials (NORM) are an increasing technical and economic concern for oil and gas production operations. Recent surveys (1) indicate that upwards of 140,000 barrels (1 barrel = 42 gallons) of NORM wastes are generated annually. In addition to this annual production of NORM waste, nearly 10,000,000 barrels of NORM, which have been produced since the late 1980's, are already being stored at numerous sites throughout the Permian basin and the gulf coast. The average cost for disposal of NORM wastes is currently between 200 to 600 $/barrel, exclusive of transportation costs. Thus the annual clean-up costs may be as high as $84,000,000 with the total cost for disposal of the accumulated wastes in excess of $2 billion.

The Department of Energy's Office of Fossil Energy and BPF, Inc. are co-funding a project that could reduce the cost of cleaning up NORM wastes while providing a simple effective disposal option for producers which eliminates the need for transportation of NORM from the production site. The primary goal of the project is the demonstration of a cost effective, highly mobile, modular system which dissolves Naturally Occurring Radioactive Materials (NORM) accumulated during oil and gas production.

In this DOE-funded project, both bench-scale and pilot-scale demonstrations of the technology will be completed. The bench-scale tests will prove the technology concept and verify treatment and disposal of NORM-containing solids from three different sites, one in west Texas and two in southeastern New Mexico. A photo of the NORM stored at the west Texas test site is shown in Figure 1. Treatment rates approaching 1 API barrel per day of sludge are planned. The typical composition of the stored NORM sludge is shown in Table 1.

Bench-scale testing is comprised of two phases. In the first phase laboratory tests were completed which demonstrated the effectiveness of the process chemistry selected for each of the treatment steps. In the second phase, field testing of bench-scale equipment will demonstrate the ability to implement the required chemistry. This phase is currently underway and will be completed during 1996.

The pilot-scale tests will be conducted primarily at the west Texas site and will demonstrate a treatment and disposal capability of 100 barrels per day of NORM-containing sludge (approximately 25 barrels per day of dewatered solids). Pilot-scale testing will be conducted beginning in the spring of 1997 and continue for approximately one year.

In parallel with the pilot-scale testing, the bench-scale unit will be operated by BPF to conduct additional demonstrations for interested parties in an effort to establish a commercial capability at an early stage in the project.

Bench-scale Equipment

The BPF bench-scale mobile system is designed around three processing modules which allow for the treatment and disposal of NORM wastes at the lease site where the NORM is generated and/or stored. The radioactivity in these wastes is the result of radium isotopes (Ra-226, Ra-228 and their associated daughter isotopes) which co-precipitate with relatively insoluble barium and/or calcium

containing scales. This system allows these radionuclides to be dissolved into aqueous solutions which are then injected into the formation from which they originated using saltwater disposal or injection wells on or near the lease site.

In Figures 2 - 5, the bench-scale equipment is shown in operation at the west Texas site during the first series of tests:

1) The thermal pre-treatment module (Figure 3) can be used to remove the oil residue in the NORM-containing wastes making them suitable for further chemical processing.

2) The solvent extraction module (Figure 4) is used to dissolve radionuclides into various aqueous solutions suitable for underground injection. This module separately treats acid soluble and acid insoluble components of the NORM-containing wastes releasing radionuclides from the scale. Residual solids having radioactivity below regulatory concern are released for disposal by the customer. Waste solutions are injected underground at the lease site using either salt-water disposal or waterflood injection wells. These solutions are transported to the injection well using the injection trailer (see Figure 2) which consists of separate holding tanks and an injection pump.

3) The sorting/assay module (Figure 5) is used to perform volume reduction on the NORM-containing solids by separating the solids having radioactivity below regulatory concern from those which must be chemically processed using the solvent extraction module. Radioactivity is measured using gamma spectroscopy with a liquid-nitrogen cooled GaAs detector. Volume reductions of 95% are expected for sites such as abandoned pipeyards. This module is also used to perform a 100% assay of residual solids to verify that materials for release have radioactivity levels below regulatory thresholds. This module is also suitable for a variety of gamma-emitting radionuclides such as those found at low-level nuclear waste sites.

Process Description

The BPF process is designed to treat either dry materials containing NORM, such as might be found when remediating a contaminated pipe yard or lease site, or wet materials containing NORM, such as tank bottoms or sludge pits. Wet materials are currently being stored at all three of the bench-scale test sites and are the focus of the initial testing operations. The primary process steps and material flow are displayed in Figure 6.

The stored wet NORM materials are de-oiled during bench-scale either using the thermal pre-treatment module or in the solvent extraction module. Results of the bench-scale tests will determine which method will be used in the pilot-scale tests.

Volume reduction and 100% radioassay of the de-oiled and/or dry NORM-containing solids is accomplished on site using the sorting/assay module. The primary purpose of the sorting/assay step is a volume reduction of the materials which require further processing in the solvent extraction module. This is particularly useful for contaminated sites where radioactive scale has been distributed over an otherwise clean site. For tank bottoms where the radioactivity

is more homogeneously distributed, the volume reduction step can be bypassed. However, the 100% radioassay is still useful for this tank bottom NORM as a confirmation of the starting activity levels in the untreated materials. The volume reduction is accomplished by measuring the radioactivity of the soil/sludge using an EG&G Ortec Gamma Spectrometer. The soil/sludge is conveyed under the spectrometer using a specially designed computer-controlled machine which processes 2kg material increments in a continuous manner. Based on the measured radioactivity, each 2kg increment is automatically shunted to either a "hot" or a "cold" drum according to a user defined threshold. "Cold" material can then be released to the customer for disposal along with a certification and complete data record documenting the measured activity of the "cold" material released for disposal. Hot material is then processed using the solvent extraction module.

Radionuclide extraction is accomplished using a series of chemical processing steps in the solvent extraction module. In the bench-scale system the NORM containing solids are held in a reaction vessel throughout the process. Various treatment chemicals are pumped from holding tanks into the reaction vessel. The solid/chemical mixtures are agitated using stirrers for the appropriate times. Acid insoluble scales are dissolved using a proprietary barium sulfate dissolver.

These chemical steps result in the radionuclides being dissolved into solution. These solutions are collected in the injection trailer for subsurface injection using either a salt water disposal well or a waterflood injection well on the lease. No solids are ever required to be injected underground with the BPF process thereby reducing cost and simplifying the permitting process for disposal.

Residual solids are removed from the reactor vessel and a 100% radioassay is performed using the sorting/assay module. This provides for verification that the remaining solids have activity levels below the regulatory limits defining NORM. The solids are then returned to the customer for disposal.

Laboratory Tests

The process chemistry required for bench-scale testing was confirmed in the laboratory on approximately 1 liter solid/liquid mixtures. Laboratory analysis of NORM samples taken from the storage drums in the field were conducted. These results are displayed in Table 1. The general composition of the NORM varies considerably from site to site. The west Texas site is primarily sand grains which are mixed with organic sludge and individually coated with scale. The New Mexico sites are mostly acid-soluble scales and organic residues. However the radioactivity is contained almost entirely in the residual acid-insoluble solids at both sites. Thus the bench-scale process must be robust enough to allow for variations in the input materials. Each step in the bench-scale process was simulated using NORM from all three test sites and all aspects of the process chemistry were verified to be effective. Typical radioactivity reductions achieved during these trials are displayed in Table 2. The bench-scale equipment design was based in part on these laboratory results.

Bench-scale Field Tests

As of this writing, the initial round of bench-scale tests have been completed. These were conducted during the week of August 12, 1996. In these tests, the equipment check-out has been completed and the individual process steps have been verified to be effective.

Several specific accomplishments have been achieved thusfar, including:

- 250 lb. of NORM-containing sludge were processed in the thermal pre-treatment module. Almost complete oil removal was accomplished yielding dry solids suitable for further processing in the solvent extraction module.
- 300 lb. of NORM-containing sludge were processed in the solvent extraction module. The radioactivity which initially averaged 470 pCi/g (Ra-226), was reduced to 70 pCi/g (Ra-226) (Table 3).
- The sorting/assay machine calibrations have been completed and effective sorting has been demonstrated. The machine is also proving effective for on-site measurements of in-process samples.
- Review of the preliminary economic data indicate that the process can be competitive with existing disposal practices. These estimates are exclusive of transportation costs. Transportation costs do not exist for the BPF process.

Some technical challenges have been identified during the first round of tests:

- Insufficient capability for solid/liquid separation during in-process handling. This is being corrected prior to the next round of bench-scale tests. The conceptual designs for the pilot-scale equipment have solid/liquid separation as an integral step in the material flow path.
- Dust generation has been an issue when using the sorting/assay machine on dry materials. The bench-scale system has been modified using polyethylene sheeting to reduce the migration of dust. Additional provisions for vacuum collection are being made prior to the next round of tests. The pilot-scale system will contain the capability of processing wet materials which will eliminate the problem entirely.

Near-term Goals

Argonne National Laboratory, operating under a separate contract with DOE is supporting the NEPA compliance activities for the pilot-scale process. DOE has currently determined that an environmental assessment is appropriate for pilot scale. Argonne is currently conducting a risk assessment of the process using measurements which will be taken during the bench-scale tests. In the next round of tests, scheduled to begin September 30, 1996, radiation exposure, air emission and time motion measurements will be taken in support of the risk assessment. Argonne is also conducting additional groundwater modeling studies to verify the negligible groundwater risks from hypothetical injection well casing failures (2).

The next round of tests scheduled for early October 1996 will exercise the process as a complete system. An additional 400 lbs of sludge will be processed during these tests. The data required for a detailed economic analysis of the process will be collected along with the risk analysis data described above.

The sorting/assay module is designed to process up to 2.5 tons/hour of NORM-containing materials. The bench-scale unit, while capable of moving soil/sludge through the detector at these rates, does not yet have the automated material handling equipment necessary to achieve the design throughput. The auger feed and larger staging hoppers required to complete the module will be added to the final system prior to pilot-scale testing.

Summary

Treatment and disposal of NORM-containing materials are a continuing issue for oil and gas production operations. BPF is demonstrating a mobile, cost-effective system for the on-site treatment and disposal of NORM-containing wastes. The bench-scale equipment modules have been staged to the field and preliminary testing is underway. Initial results have shown that the proposed process steps are effective in dissolving radionuclides from the treated solids into aqueous solutions suitable for sub-surface injection. Radioactivity levels below regulatory concern have been achieved in the residual solids treated using the BPF process. A risk analysis of the process is underway in support of the NEPA compliance activity for pilot-scale testing. Continuing tests are planned for the remainder of 1996. Demonstration of commercial clean-up capabilities will follow shortly thereafter. Pilot-scale testing is scheduled to begin in the spring of 1997 and continue for one year thereafter.

Acknowledgments

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2.) G. P. Williams, K. P. Smith, D. L. Blunt, and C. L. Tebes, Modeling of NORM Injection in a Layered Geologic System, Proceedings of the 1995 API/GRI NORM Conference, pg. 109, American Petroleum Institute, February 1996.

Tables

Test Site	Moisture Content	Water Soluble Fraction	Acid Soluble Fraction	Organic Fraction	Acid Insoluble Fraction
West Texas	21.54	2.83	3.51	8.50	63.62
New Mexico #1	18.75	0.62	40.32	18.46	21.85
New Mexico #2	16.15	1.23	57.24	19.38	6.00

Table 1. Average composition of NORM waste samples from the three test sites. All quantities are given in percent of total quantity.

Sample Description	Mass	Total Activity
	(g)	(pCi/g)
De-oiled NORM solids	50	712
Treated NORM solids (1st pass)	50	129
Treated NORM solids (2nd pass)	50	25

Table 2. Results of radiation dissolution laboratory experiments using proprietary barium sulfate dissolver.

Sample Description	Mass	Activity
	(g)	(pCi/g Ra-226)
#1 De-oiled NORM solids (dry)	218	253
#1 Treated NORM solids (1 pass)	218 + liq.	202
#2 De-oiled NORM solids (wet)	*	*
#2 Treated NORM solids (1st pass)		320
#2 Treated NORM solids (2nd pass)		70

Table 3. Initial results of radiation dissolution field experiments using proprietary barium sulfate dissolver.

Figures

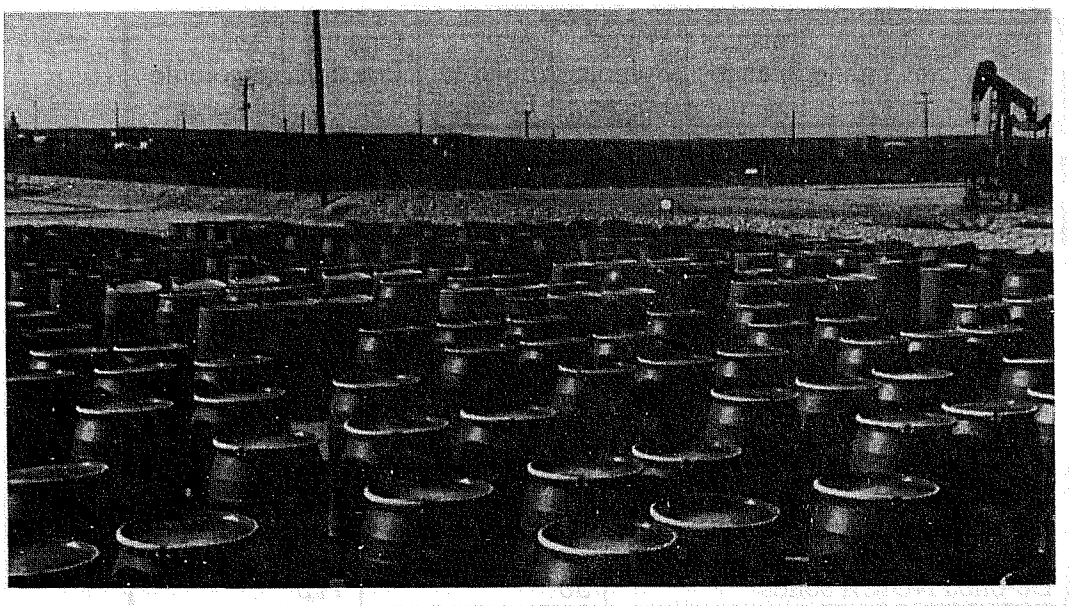

Figure 1. NORM Storage Area at the West Texas Bench-scale Test Site.

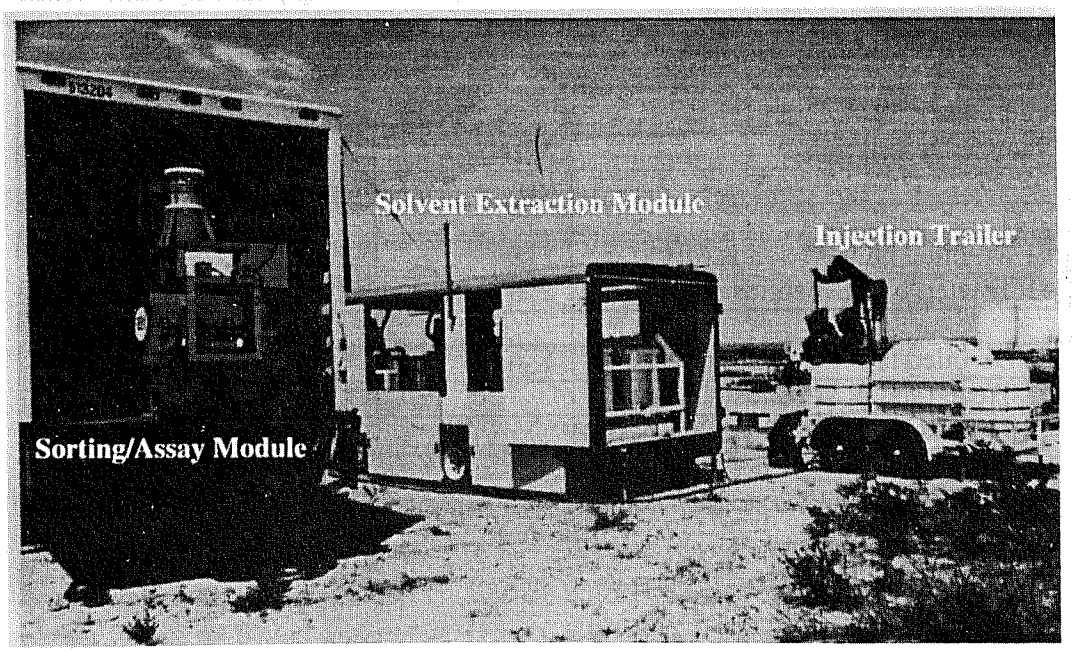

Figure 2. Field Installation of the BPF NORM Treatment and Disposal System Hardware.

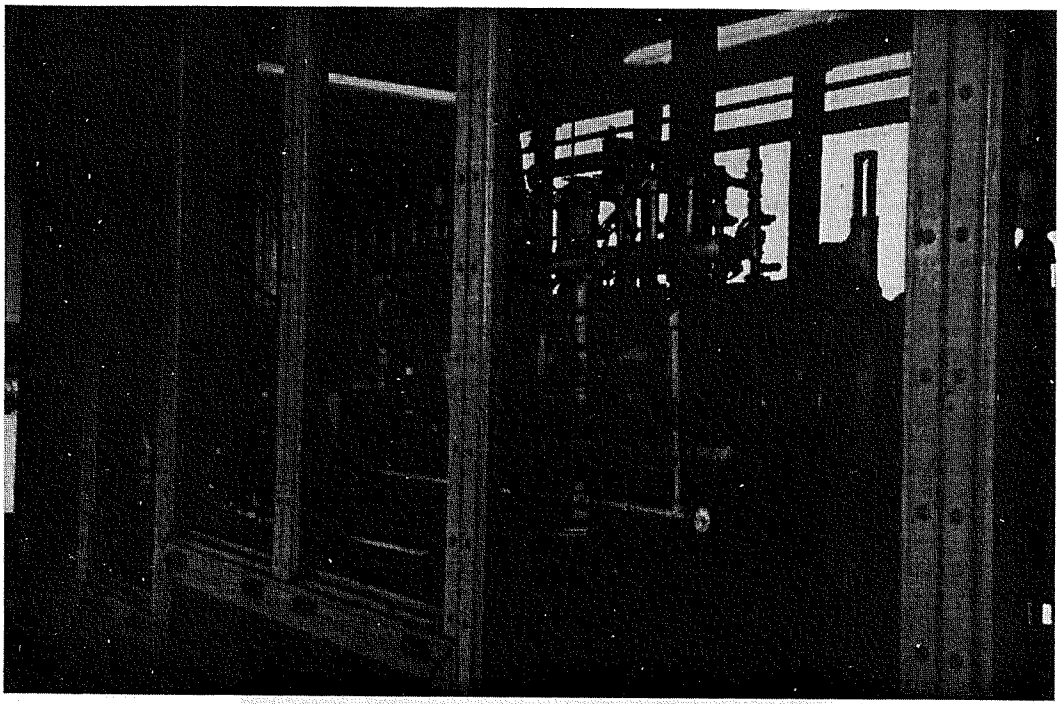

Figure 3. Thermal Pre-treatment Module used for Bench-scale Testing.

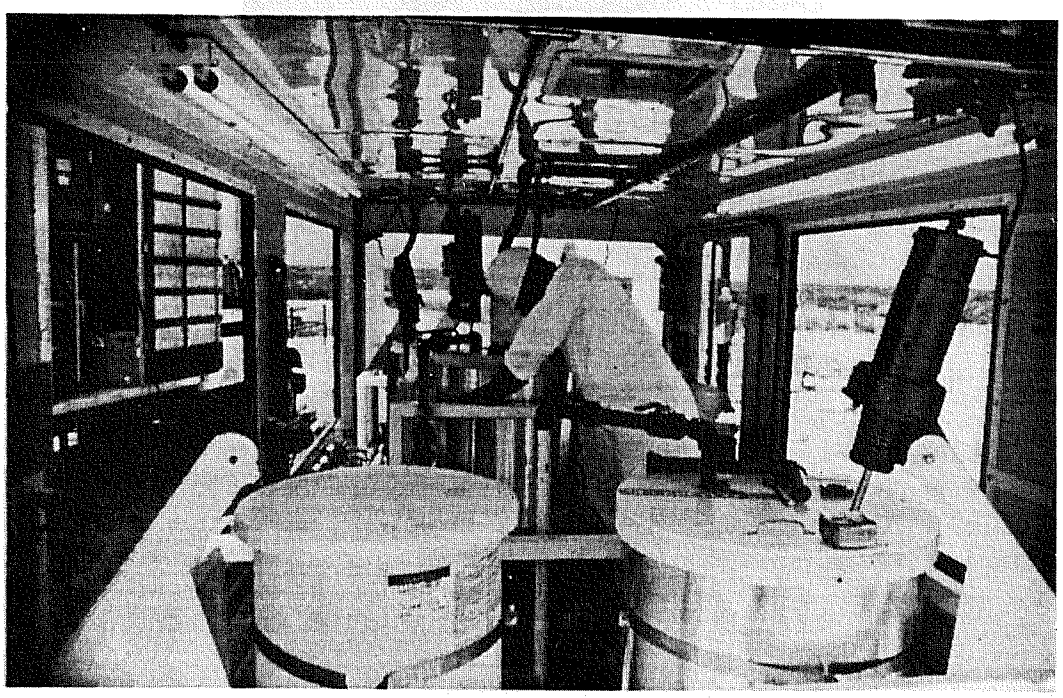

Figure 4. Interior of the Solvent Extraction Module used for Bench-scale Testing.

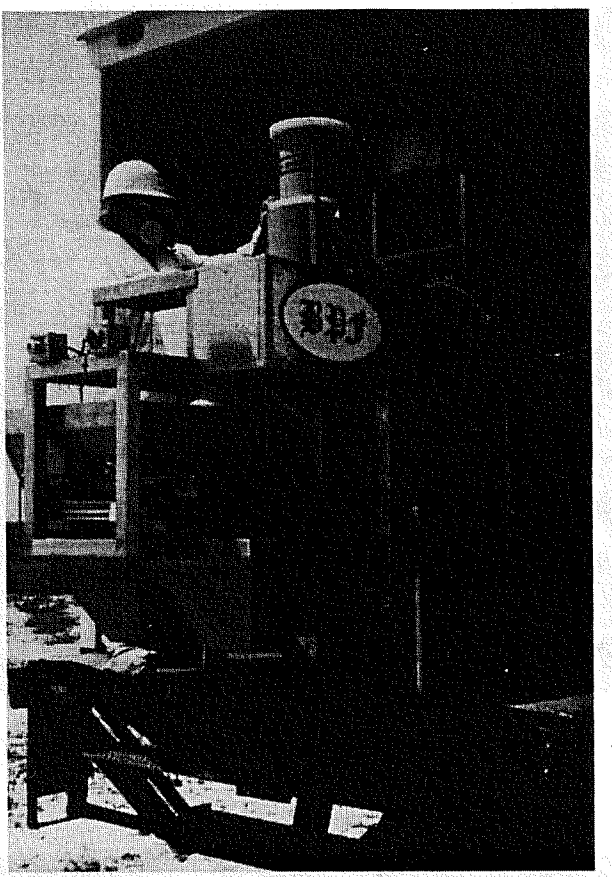

Figure 5. Sorting/Assay Module used for Bench-scale Testing.

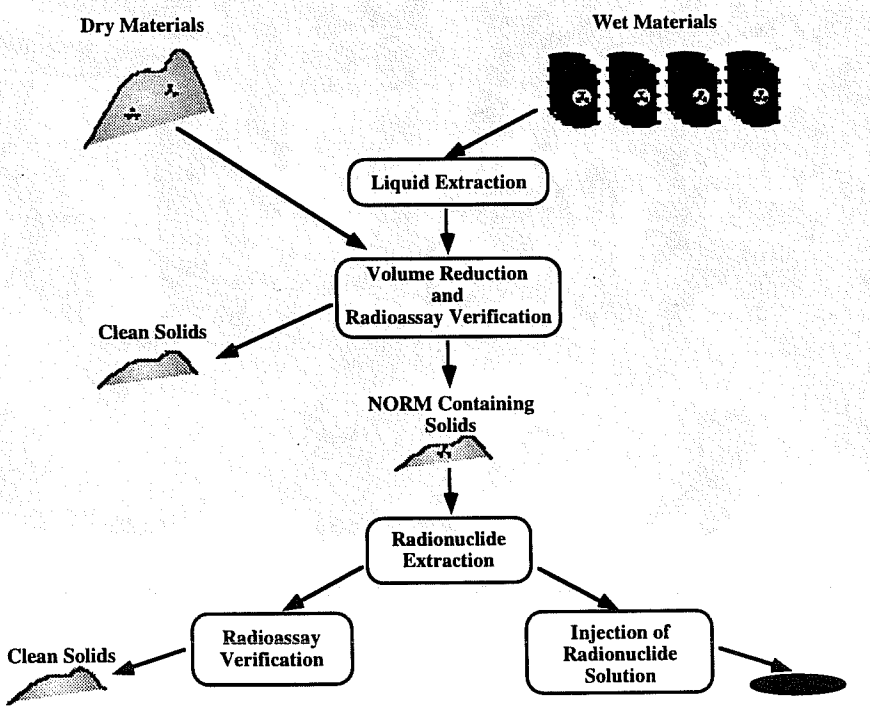

Figure 6. Process steps and material flow for the BPF NORM treatment and disposal process.

Pollution Prevention and Waste Minimization

An Evaluation of the Microtox Solid Phase Test for the Screening of Hydrophobic Materials

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The Microtox® toxicity analyzer was investigated as a quick method for the screening of hydrophobic base fluids used in drilling muds. The Solid Phase Test, developed by Microbics Corporation, assesses sediment toxicity by exposing bio-luminescent bacteria directly to the material being tested. In order to test the four materials selected for this study: diesel, C1416 linear alpha olefin, C1618 internal olefin and a low-toxicity mineral oil, a sediment had to be chosen which showed basically no toxicity. The sediment chosen was a blasting sand with a particle size range of approximately 75 to 425 microns. Each test material was mixed with the sediment at concentrations of 1, 2, 4, and 8% by weight and tested for toxicity. Four replicates were run at each concentration and the resulting data was analyzed. Based on the test results, the Solid Phase Test shows limited promise as a screening tool for water-insoluble base fluids.

INTRODUCTION

Today there are many concerns about the discharge of industrial waste into the aquatic environment. Concerns about the discharge of these materials have led to the development of many different testing techniques aimed at determining the toxicity of these materials. In the drilling industry some of the most widely used ecotoxicolgical tests are bioassay tests. These test use certain organisms as gauges to determine the toxicity of products used in drilling fluids. The main test used for this purpose in the United States is the 96-hr Acute Mysid Bioassay test.[1] This test was included as a permit requirement in the mid-1980s as a way to determine if the drilling fluids being used at the time were safe for discharge into the marine environment.

At the time the protocol for this test was developed, water-based drilling fluids (WBMs), which use water as their continuous phase or base fluid, were the only types of drilling fluids that were able to be discharged into the aquatic environment. The mysid bioassay test is well suited for testing materials which are soluble in water and may have water-column effects.

In the early 1990s, synthetic-based drilling muds (SBMs) were introduced as an environmentally sound replacement for oil-based drilling fluids. SBMs used the newest technologies to provide a drilling fluid with the drilling capabilities of oil-based muds without the priority pollutants which are associated with them. The new SBM use a synthetic, or man-made, liquid as its continuous phase or base fluid unlike the WBMs which use water as the continuous phase. The problems with these new fluids are their lack of solubility and the fact that the regulatory test required for the Gulf of Mexico relied on technology developed to test water soluble materials.

There are, as mentioned earlier, many different types of bioassay tests available. One of these tests which may be able to overcome the problems in testing the SBM base fluids is the Microtox Solid Phase Test. This test relies on bioluminescent bacteria, *Photobacterium phosphoreum*, as its test organism. This tests seems to have the following advantages over the 96-hr mysid test.

1) The Solid Phase Test may give a better idea of the effects of the benthic community which is important since the discharge of SBM is more likely to impact the benthos instead of the water column.

2) The test organisms, bioluminescence bacteria, are more likely to be exposed to the test material, unlike the mysid bioassay where the main portion of the test material is not introduced into the test.

3) The Solid Phase Test has a faster turn around time and is less expensive as compared to the 96-hr Mysid test.

4) The organisms are highly sensitive to pollutants.

The Solid Phase Test is a modified version of the basic Microtox Test in which a sediment can be tested in a quick and inexpensive manner. The Solid Phase Test was developed to test field sediments for pollutants. Therefore it seemed logical to use a sediment as a medium to test certain hydrophobic materials such as the synthetic fluids used in some drilling fluids. In the Solid Phase Test, a sediment of known toxicity could be spiked with the material that was to be tested. Since the materials are hydrophobic, the spiked sediment would allow the test organisms to come in contact with the material and allow its toxicity or lack there of to be determined.

The first goal was to develop a base sediment that would not interfere with or mask the toxicity. The second goal was to determine if this type of test was able to be used to screen certain hydrophobic materials. The third goal to measure dose response relationships and repeatability of test results.

SOLID PHASE TEST METHODS AND MATERIAL

The analyzer used for this study was the Microtox model 2500. A constant temperature water bath was needed to keep the sample concentrations at 15°C. A 10-gal aquarium with a chiller served as a constant temperature water bath. The materials to be tested were as follows. C1618 internal olefin (IO), C1416 linear alpha olefin (LAO), diesel, and a low-toxicity mineral oil. **Figure 1** is a schematic of the setup.

Fifteen Solid Phase test tubes are placed into a test-tube rack which has been placed into the constant temperature water bath. 15 cuvettes are placed into the wells on the model 2500 analyzer. One cuvette is placed into the reagent well and filled with 1 mL of reconstitution solution. Solid Phase test tubes 1-14 are filled with 1.5 mL of Diluent.

Next an appropriate amount of the test sediment is placed into a 50 mL beaker; for example if 1% of the test material is to be tested then 9.90 g of dry sediment is placed into the beaker and 0.10 mL of the test material is added to the sediment. The spiked sediment is then stirred with a stainless steel spatula until the mixture is homogeneous. 7 g of the homogeneous sediment mixture is then placed into another clean 50 mL beaker and a Teflon stir bar is added. 35 mL of Solid Phase diluent is then added to the sediment and the slurry is placed onto a magnetic stir plate and stirred for 10 min making sure that the stirring vortex is approximately 50% the depth of the beaker. After stirring for 10 min, two 1.5 mL samples of the slurry are removed while the slurry is still being stirred. The 1.5 mL samples are taken at approximately 2 cm from bottom of beaker using an adjustable pipette. 1.5 mL of the slurry are added to the existing 1.5 mL Solid Phase Diluent in the test tube #14 and the empty test tube #15.

Additional dilutions are made by transferring 1.5 mL of the material in test tube 14 to test tube 13 and 13 to 12 and so on until you get to test tube 4. Test tubes 1, 2, and 3 only contain 1.5 mL of Solid Phase Diluent and are used as controls. After 1.5 mL is added to test tube 4 and mixed 1.5 mL is discarded.

The test tubes are then allowed to equilibrate to 15°C by sitting for 10 min in the water bath. After 10 min has elapsed a bottle of reagent is reconstituted with the 1 mL of reconstitution solution that was placed in the reagent well. After mixing the reagent and reconstitution solution with a 0.5 mL pipette, 0.2 microliters are pipetted into each of the Solid Phase test tubes and mixed with a 0.5 mL pipette. Filter columns are placed into each of the test tubes making sure not to come in contact with the solution. These solutions are allowed to sit for 20 min with the bacteria in contact with the test solution. After 20 min the filter columns are pressed down and the solution is filtered into the filter column. The filter column filters out every particle larger than 100 microns. 0.5 mL of the filtered solution is pipetted from the 15 test tubes into the cuvettes which have been placed in the wells on the analyzer. When all the cuvettes have received 0.5 mL of solution light readings can be taken.

The first control, cuvette 1 is placed into the read well and the light span is adjusted to give a reading of 95. All of the light readings will be based on the setting of 95 as customary with Microtox operations. The resulting light readings are entered into the Microtox Data Capture and reporting program. This program calculates an EC_{50}, which is the sample concentration which reduces the bacterial light output by 50%, or gamma equals 1.0. Four separate replicates were run on each of the test materials at 1, 2, 4, and 8% by weight to determine if repeatability was possible.

RESULTS

Microbics Corp. the developer of the Microtox system ran some preliminary tests using cuttings coated with the synthetic-based fluid to determine if the bacteria used would be recoverable after exposure to the test material, (were not lost to adhering to the spiked sediment). These initial test showed that the bacteria were recovered and that this test was viable when used in this manner.

Since this test is primarily being used as a screening tool, the sediment used must have a low toxicity and be easy to obtain. The three sediments selected were:

1. 10% sand (Specialty Sand #5), 40% silt (Rev Dust), and 50% Clay (Xact)
2. 50% Sand (Specialty Sand #5), 50% Clay (Xact)
3. 100% Sand (Specialty Sand #5)

In chosing a test sediment, we wanted to reproduce the grain size range of the sediment of the Gulf of Mexico.[2]

Sediment #1, without any base fluid, was our attempt to reproduce this sediment. The initial Solid Phase Test on this sediment gave an EC_{50} of 0.70% (7,000 ppm). A problem with the makeup of this sediment was the affinity of the clay and silt to pass through the 100 micron filter and stay suspended in the diluent and thus causing color interference with the light readings from the bacteria. Sediment #2 had an EC_{50} of 0.95% (9,500 ppm) and also caused interference due to the suspension of the fine clay particles. Sediment #3 showed no toxicity at the same concentrations as sediments #1 and #2. With these results and other studies done on the subject of sediment composition using the Microtox Solid Phase Test[3] it was decided that sediment #3, 100% Specialty Sand #5, would be used as the base sediment. The grain size analysis of sediment #3 showed that about 98% of the grains fall between 75 - 425 microns in size.

Four replicates of each sample concentration were tested to determine if repeatability was obtainable. The samples included C1618 IO, C1416 LAO, Diesel and a low toxicity mineral oil. Each material was run at 1, 2, 4, and 8% by weight in sediment #3. The following results were found for each sample.

C1618 IO showed a steady increase in toxicity as the amount of test material was increased (**Figure 2**). The coefficient of variability for the four concentrations tested on the C1618 IO ranged from 17.6 to 26.8% (**Table 1**).

C1416 LAO also showed a steady increase in toxicity with an increase in amount of test material (**Figure 3**). The coefficient of variability which was higher for this material than it was for C1618 IO ranging from 13.6% to 29.4% (**Table 2**).

The low toxicity mineral oil did not have a good toxicity response curve (**Figure 4**). Most of the concentrations tested showed relatively low toxicity or EC50s greater than the highest concentration being tested, 19.787%. The coefficient of variability was extremely high for the replicates run on the low toxicity mineral oil (**Table 3**). This is most likely due to the extrapolation of data by the Microtox statistical program. A try at obtaining a calculated EC_{50} was attempted by increasing the highest concentration of spiked sediment to 39.574%. This was accomplished by reducing by half the amount of diluent in the sediment slurry, 17.5 mL of diluent instead of the normal 35 mL. With the increased ratio of sediment to diluent the slurry became turbid and color interference occurred. A data inversion occurred in the 4% test concentration with a decrease in the toxicity (**Figure 5**).

The diesel had a steep decrease in toxicity and then flattened off at 2-8% concentrations (**Figure 5**). The coefficient of variability was high for diesel ranging from 42.9%-59.3% (**Table 4**).

There was one controllable variable in this project and that was the concentration at which each material was tested. A regression analysis was run on each material to determine if the test concentration was a predictor of toxicity. C1618 IO had a regression equation of C1618 = 3.50 - 0.344 x concentration. The analysis did show that concentration was a significant predictor of the toxicity of C1618 IO (P = 0.000 F = 30.96). The regression equation for C1416 LAO, 13.4 - 1.53 x concentration, also showed that the concentration was a significant predictor of toxicity (P = 0.000 F = 22.9). The regression equation for diesel, 0.0625 - 0.00823 x concentration, showed that concentration was a significant predictor of toxicity (P=0.036, F = 5.41). The regression equation for the low toxicity mineral oil, 53.2 - 2.15 x concentration, was not a significant predictor of toxicity (P = 0.524, F = 0.43). This was due to the inversion that occurred in the data at the 4% test concentration.

OBSERVATIONS & CONCLUSIONS

Sediment #3 seemed to be a good choice in that it was easy to obtain, consistently showed no toxic response at tested concentrations and did not interfere or mask the toxicity of the test materials.

Based on the toxicity dose response curves of the tested materials there is a correlation between the amount of material introduced and the toxicity to the test organisms for the C1618 IO, C1416 LAO and diesel but not for the low toxicity mineral oil. The same response to increasing concentration was seen statistically when regressing concentration vs. toxicity. The poor response curve and lack of correlation for mineral oil is most likely due to poor sensitivity of this test to mineral oil at any of the concentrations we tested.

When looking at repeatability between replicates of the same materials, the coefficient of variability gave mixed results ranging from a low of 13.6% to high of 80.1%. The variation in the coefficient of variability was most likely due to differences in the actual amount of tested materials exposed to the test organisms. These differences were due to the insolubility of the material and the amount of material that did or did not adhere to the sediment and floated on the top of the test solution. A solution to the coating of the sediment with the test materials may be to mix the sediment and test material together and then roll the mixture for a predetermined time to ensure some sort of homogeneity or better adherence.

During dilution of the test concentrations in the Solid Phase test tubes only the three highest concentrations, tubes 12 - 15, have any sediment in them. Since the sediment is used as a carrier of the test material the lower concentrations are dependent on solubility of the test material.

Overall the assessment of the Solid Phase Test is that it is limited in the range of materials that can be tested, being better at testing materials with high solubility.

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3. Microbics Corporation, *Microtox M500 Manual, A Toxicity Testing Handbook*, version 3 (9-12-1994) 4/41-4/49.

Microtox is a registered trademark of Microbics Corporation.

The views expressed in this paper reflect those of the author and are not necessarily those of M-I Drilling Fluids L.LC.

Table 1
Statistical data for C1618 IO

Concentration (%)	Mean	Standard Deviation	Coefficient of Variability	Lower Limit	Upper Limit
1	3.585	0.6292	17.6	2.653	4.517
2	2.790	0.6798	24.4	1.858	3.722
4	1.415	0.2650	18.7	0.483	2.347
8	1.058	0.2830	26.8	0.125	1.990

Table 2
Statistical data for C1416 LAO

Concentration (%)	Mean	Standard Deviation	Coefficient. of Variability (%)	Lower Limit	Upper Limit
1	15.510	2.120	13.6	14.578	16.442
2	8.333	2.215	26.6	7.400	9.265
4	3.753	0.976	26.0	2.820	4.685
8	2.905	0.853	29.4	1.973	3.837

Table 3
Statistical data for low toxicity mineral oil

Concentration (%)	Mean	Standard Deviation	Coefficient. of Variability (%)	Lower Limit	Upper Limit
1	47.1	36.6	77.7	46.155	48.020
2	40.5	29.5	72.8	39.525	41.390
4	64.2	51.4	80.1	63.243	65.107
8	28.82	16.03	55.7	27.883	29.747

Table 4
Statistical data for diesel

Concentration (%)	Mean	Standard Deviation.	Coefficient. of Variability (%)	Lower Limit	Upper Limit
1	0.0908	0.054	59.3	– 0.841	1.023
2	0.0138	0.006	42.9	– 0.918	0.946
4	0.0137	0.008	57.1	– 0.919	0.946
8	0.0080	0.004	50.0	– 0.924	0.940

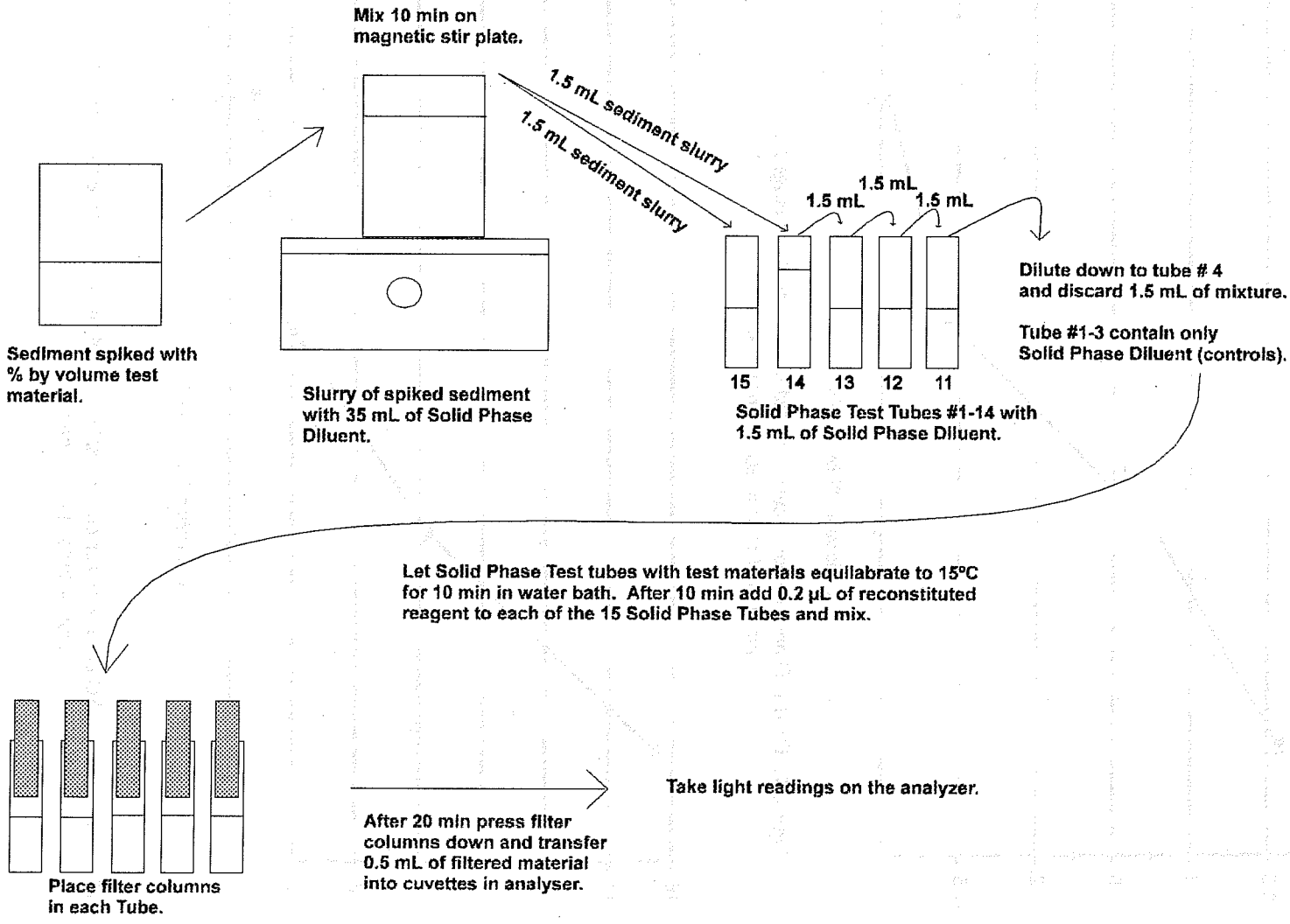


Figure 1. Solid Phase Test schematic.

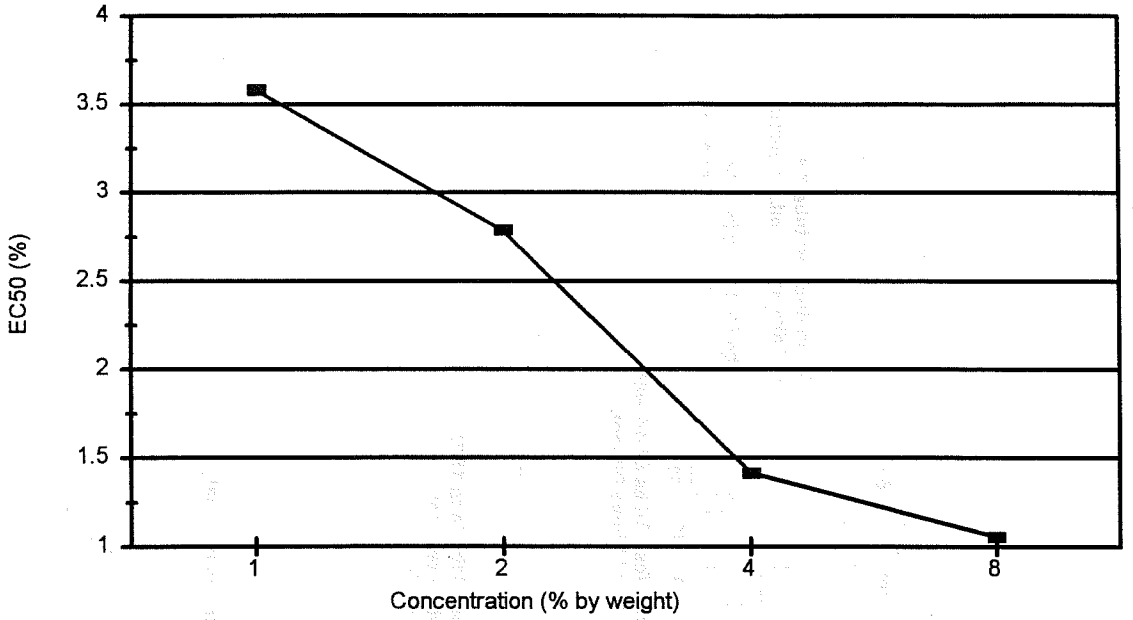


Figure 2. C1618 IO dose response curve created by plotting the average EC_{50} value from 4 tests at each concentration.

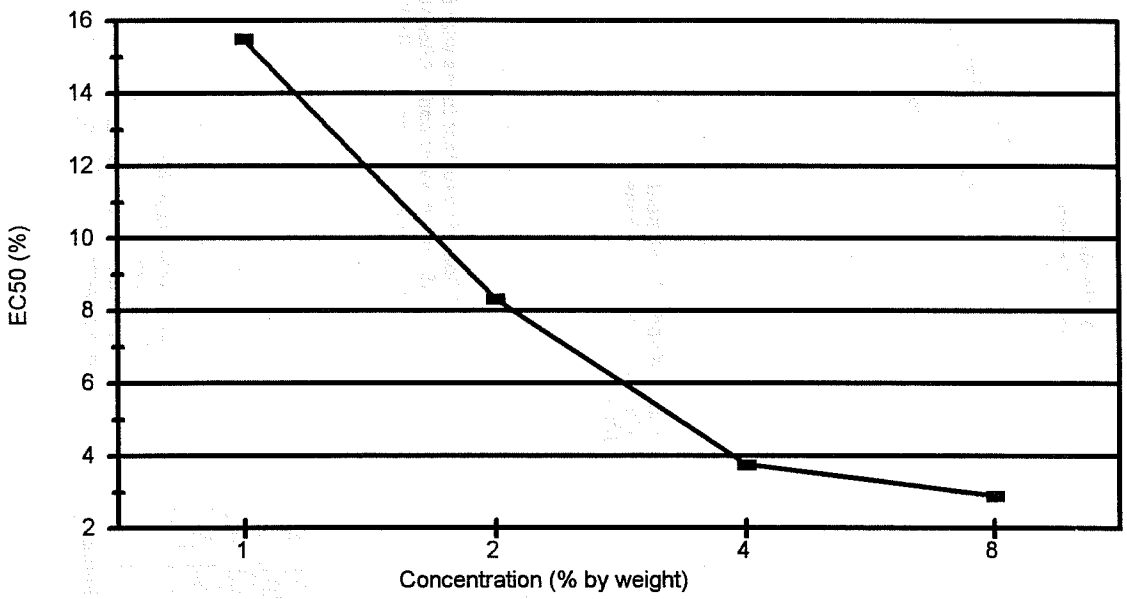


Figure 3. C1416 LAO dose response curve created by plotting the average EC_{50} value from 4 tests at each concentration.

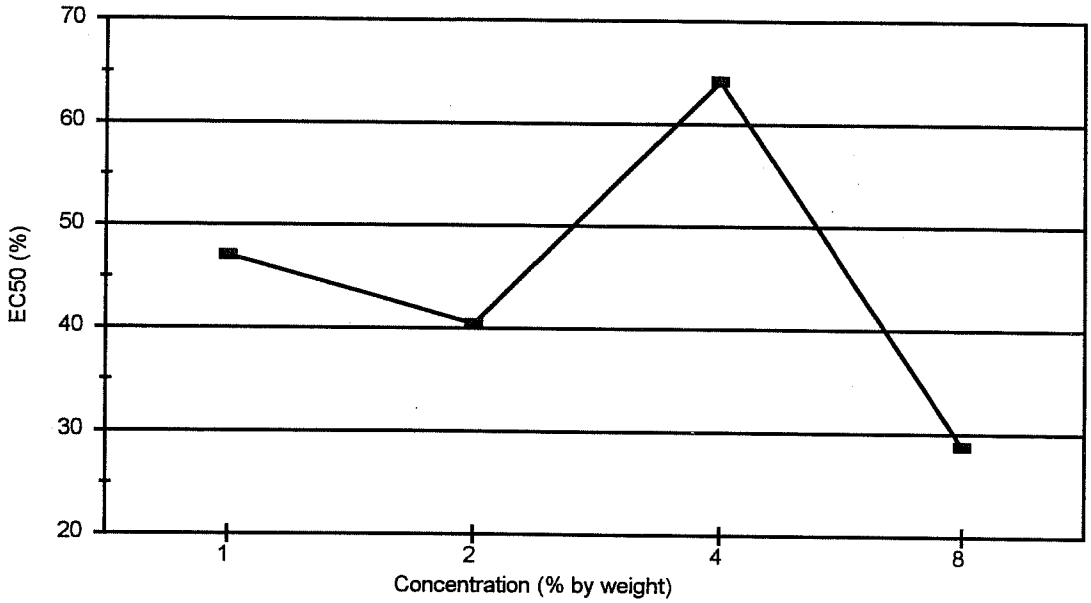


Figure 4. Low-toxicity mineral oil toxicity curve created by plotting the average EC_{50} value from 4 tests at each concentration.

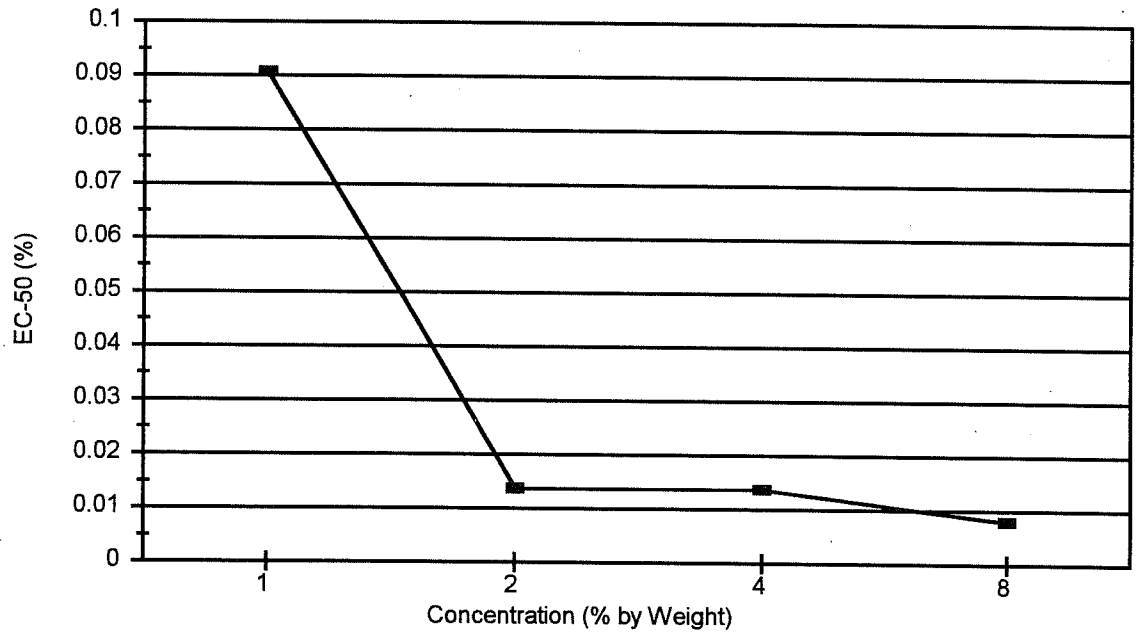
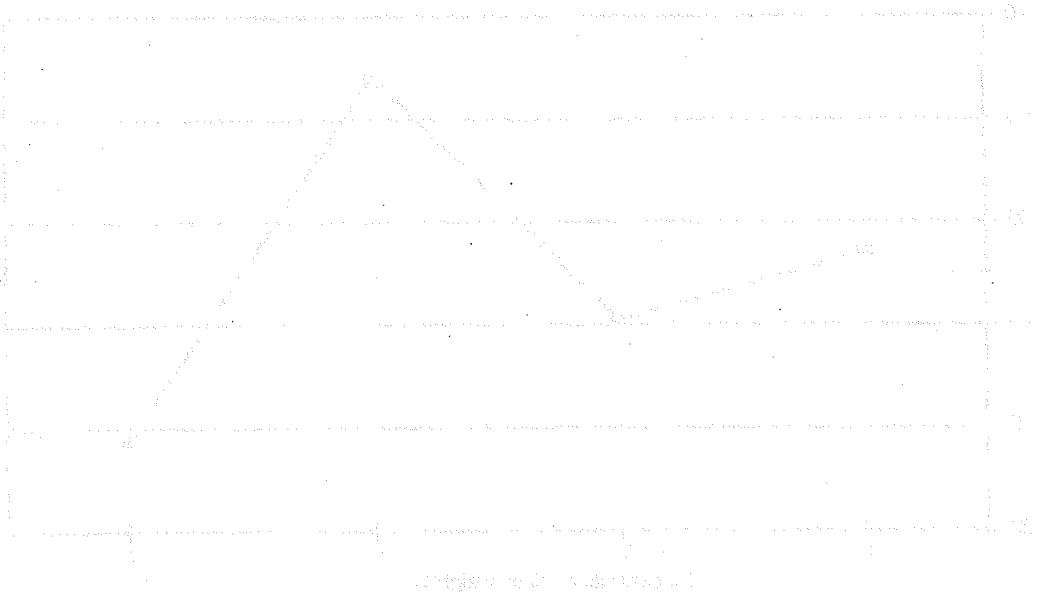
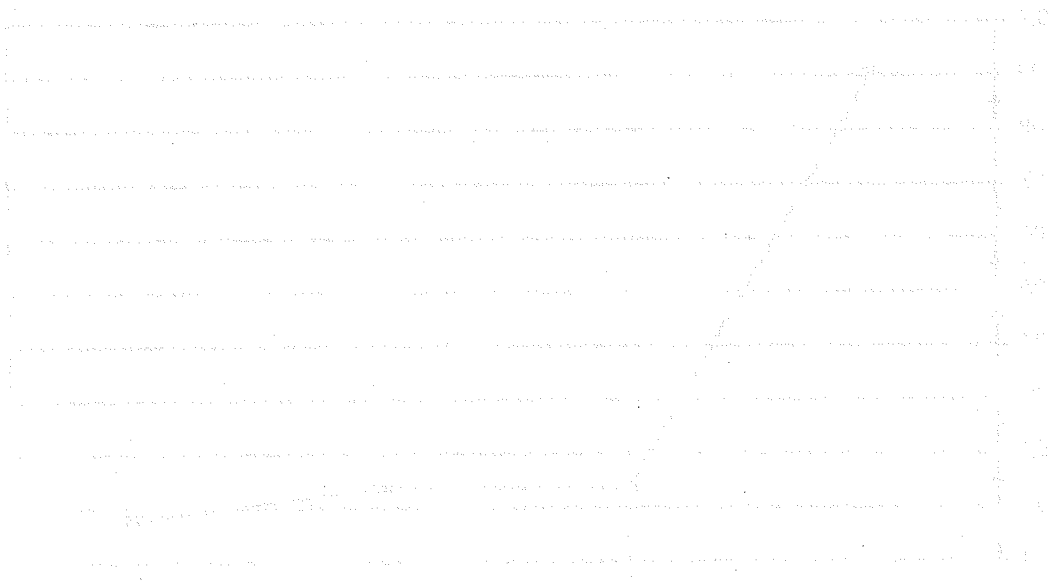


Figure 5. Diesel toxicity curve created by plotting the average EC_{50} value from 4 tests at each concentration.





Spray Polyurea Coatings as Containment Liners

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Environmental regulations are forcing companies to consider the use of secondary containment in petrochemical storage, processing, and production facilities. Secondary containment involves placing an impermeable barrier between the stored fluid and soil, surface water, and groundwater, which may be contaminated by accidental releases.

Two common methods of achieving compliance with secondary containment regulations are the use of plastic liners (sheet goods), or coatings. Sheet goods must be seamed together to form a continuous, impermeable membrane, and they must be attached mechanically to penetrations such as tanks. These seams and attachments offer potential avenues for leakage. Many chemically resistant coatings are rigid, with the potential for cracking, leading to failure. Some coatings do not stand up well to traffic, and some contain potentially toxic solvents.

This paper will discuss the use of spray polyurea coatings as containment liners. Polyurea coatings harden in less than ten seconds, require no seams, and attach directly to penetrations such as tank rings or pipes. These tough, flexible coatings are resistant to cracking, and stand up well to traffic. In addition, polyurea coatings contain no solvents, meeting air quality regulations.

Polyurea coatings can be used in the petroleum industry as secondary containment coatings in storage facilities, in field drilling operations as pond liners, as tank liners to prevent corrosion, and to protect pipes from corrosion by cooling water. The use of polyurea coatings enables the facility owner to minimize downtime, and to reduce the risk of leaks which result in environmental damage.

ENVIRONMENTAL REGULATIONS

The storage and handling of hazardous wastes are regulated by the Federal Government. Under Federal regulations, some form of secondary containment must be used in areas where new tanks are used to store waste, or in all areas with extremely hazardous materials. Options include tank liners, double walled tanks, or vaults. External liner systems must contain 100% of the capacity of the largest tank in the storage area plus the water generated by a 25-year, 24-hour rainfall event. These containment systems must be compatible with and impermeable to the materials stored, and must not contain cracks or gaps.

The Clean Water Act of 1973, and its amendments in the Oil Pollution Act of 1990 establish regulations aimed at reducing discharges of oil into surface water and onto adjoining shorelines. These regulations require facility owners who meet certain requirements to develop a Spill Prevention Control and Countermeasure Plan (SPCC Plan). Regulations in Volume 40 in the Code of Federal Regulations 112 (40 CFR 112) offer guidelines to meeting containment requirements, specifically mentioning the use of dikes, berms or retaining walls which are sufficiently impervious to contain spilled oil. These regulations do not define the term "impervious" and thus leave a great deal of leeway to companies in meeting the regulatory requirements.

Over the last several years, various states and localities have become involved in developing their own secondary containment regulations for a variety of materials, including petrochemicals, agricultural chemicals, and hazardous wastes. Examples of states which have developed their own regulations are New Jersey, New York, Florida, Virginia, Ohio, Wisconsin, and California. In some cases, these state regulations are very specific about requirements for secondary containment. For example, the State of Florida requires that synthetic liners used in secondary containment be puncture resistant, have a permeability rate to the stored material of less than 1×10^{-7} centimeters/second (cm/s), be capable of containing the liquid for 30 days, and be approved by the state Department of Environmental Protection. These regulations, unlike the vague standards issued by the Federal Government, will require the use of secondary containment in petrochemical storage facilities.

MATERIALS FOR SECONDARY CONTAINMENT

There are a number of products which are used as impervious barriers in secondary containment applications. They are: (1) Concrete or asphalt, (2) Liners or sheet goods, and (3) Coatings. Each has advantages and disadvantages, which are discussed below.

Concrete is widely used in secondary containment. However, concrete tends to crack and deteriorate over time, increasing the prospects of contamination of soil or water by a leak. In addition, concrete is relatively expensive to install. Finally, certain chemical products may cause corrosion of concrete, again reducing the integrity of the concrete as an effective barrier to contamination by leaks or spills. Asphalt can also be used in secondary containment, but it, too, tends to degrade over time, and it is not chemically resistant to hydrocarbon spills.

Plastic liners, or sheet goods, are made from materials such as high density polyethylene (HDPE), polyvinylchloride (PVC), chlorosulfonated polyethylene (Hypalon), and composites of membranes and reinforcement materials (XR-5). These products offer good chemical resistance, and are generally low to moderate in cost. However, these materials require the construction of a seam between sheets in order to form a continuous membrane. Such seams offer potential paths for leakage. In addition, this type of liner must be mechanically attached or "battened" to penetrations such as walls, tank rings, or pillars, and must be "booted," or fitted around pipes and conduits. These processes are sometimes difficult and time consuming. Areas containing boots or battens provide the most likely paths for leaks to occur. Finally, many liners expand and contract with changes in temperature, sometimes as much as 3%. This may require the liner to be covered with soil to reduce temperature extremes, making leak detection difficult. If a spill does occur, the covering material needs to be removed and treated.

A wide variety of coatings may also be used in secondary containment. Examples of such materials include epoxies, polyesters, polyurethanes, and polysulfides. Coatings can be placed on almost any substrate, including concrete, steel, and even in earthen areas. These products, too, have drawbacks. Many chemically resistant coatings tend to be rigid, inflexible materials. If substrate movement occurs (for example, the expansion and contraction of concrete with temperature), these stiff coatings may crack and fail to provide an impermeable barrier. Some coatings cannot be applied under adverse weather conditions, including extreme heat and cold. Polyurethane coatings, for example, will react with surface and atmospheric moisture to form undesirable

byproducts. Many coatings require long cure times, leading to excessive downtime for critical facilities. Some coatings do not stand up well to traffic over long periods of time. Finally, many coating products contain solvents, which may be regulated under air pollution control ordinances, and may pose a workplace hazard.

Because of the shortcomings of the materials discussed above, there appears to be a need for a product which meets regulatory requirements for secondary containment while addressing the problems associated with other containment barriers.

SPRAY POLYUREA COATINGS

Spray polyurea coatings were originally developed by Texaco Chemical Company (now Huntsman Corp.) in the late 1980's. Polyurea, which is chemically related to polyurethane, was originally developed for the automotive industry to manufacture lightweight, tough, flexible automobile parts such as bumper fascia. These formulations were modified slightly to yield a product which can be sprayed to form a coating. Polyurea coating systems address many of the problems associated with the containment barrier linings discussed above.

Polyurea systems are two component, 100% solids products which set to dry in less than 20 seconds after mixing to form tough, impermeable membranes. Polyurea coatings provide a seamless barrier against chemical spills when sprayed on concrete, asphalt, geotextile, or steel. They may be sprayed directly on tanks, tank rings, pipes, and other penetrations without booting or battening. Thus, the number of avenues for potential leaks are reduced. These coatings can be formulated as highly flexible materials which will bridge cracks in concrete and accommodate substantial substrate movement. They remain flexible and tough at temperatures as low as -60° F. In addition, they do not expand and contract significantly with temperature fluctuations, and they offer excellent resistance to ultraviolet radiation (UV radiation). As a result, polyurea coatings can be left exposed with no soil cover while still retaining their performance advantages. Finally, polyurea coatings stand up well to foot and light vehicle traffic, and with proper design, can accommodate larger loads as well.

Polyurea coatings offer advantages in application as well. Because battens are not required to secure the polyurea coating to penetrations, significant savings in installation time may result. The rapid cure time of

polyurea coatings means that coated areas can often be safely returned to service within hours of coating application, resulting in reduced facility downtime. Unlike other coatings like epoxies, polyurea systems have a relatively consistent cure time over a wide range of temperatures. This means that polyurea coatings can be applied in a variety of temperatures ranging from below freezing to above 100° F with little change in dry time. Unlike its close relative, polyurethane, the chemistry of polyurea reduces the reaction of the coating components with moisture in the air or on the substrate. Polyurea may therefore be used in a wide range of atmospheric conditions where humidity or surface dampness may preclude the use of moisture sensitive coatings.

APPLICATIONS FOR POLYUREA COATINGS

Polyurea coatings have found application in a wide variety of areas. These can be broadly grouped in three categories: (1) Primary or secondary containment coatings, (2) Corrosion prevention, and (3) Abrasion prevention. Examples of each application area are given below:

1. Primary or secondary containment:
   - Pond liners
   - Dike liners
   - Liners in double bottom storage tanks
   - Tank liners

2. Corrosion prevention
   - Clarifiers in wastewater treatment plants
   - Tank liners for effluent streams
   - Effluent holding ponds
   - Pipe interior coatings
   - Manhole coatings

3. Abrasion prevention
   - Conveyer belt coatings
   - Floor coatings
   - Coatings to prevent erosion by particulates

PHYSICAL PROPERTIES OF POLYUREA COATINGS

As is the case with any coating or lining material, a number of different tests are run on polyurea coatings to determine their suitability for use in the applications listed above. Table I shows physical properties of polyurea coatings. These test results show that: (1) Polyurea coatings remain elastomeric at temperatures as low as -60° F (Mandrel Bend Test). (2) Polyurea coatings offer good tear strength and puncture resistance. allowing the coatings to be used in areas with heavy foot or vehicle traffic. (3) The coatings retain their physical properties after the equivalent of 20 years of exposure to UV radiation as shown in the QUV Weatherometer test. This means that a soil cover is not needed.

Table II shows a comparison of some of the physical properties of polyurea coatings with those of other commonly used coatings and lining products. The comparative data indicate that: (1) The elongation of polyurea coatings exceeds that of epoxies, polyurethanes, and polysulfides. It's high elongation allows the polyurea coating to bridge cracks in concrete which form as a result of substrate movement, preserving the integrity of the coating as a barrier against spills. (2) The puncture resistance of polyurea exceeds that of polysulfide and HDPE. Polyurea and polyurethanes are anticipated to perform well in areas of traffic or where puncture is possible. (3) Polyurea does not expand and contract as the ambient temperature changes to the same extend as HDPE. This means that polyurea coatings can be left uncovered and still not create a risk of tearing as temperatures change. (4) Unlike polyurethanes, the liquid components which combine to make polyurea are not sensitive to moisture. This means that polyurea can be used under adverse weather conditions including hot, humid weather and cool, damp weather.

As previously mentioned, many states are implementing regulations which require that secondary containment options must be impermeable to the liquid product being stored. The most stringent of these regulations state that the permeability of the coating or liner to the stored chemical be less than 1×10^{-7} centimeters per second (cm/s).

In addition to permeability, compatibility of the polyurea coating with the chemical product is important. Compatibility is a measure of how well the coating will withstand long term contact with the chemical. There are a number of potential measures of compatibility. One such measure is the change in coating thickness on exposure to the petrochemical product. Generally, when a coating is incompatible with a chemical, that coating will swell. This is accompanied by a significant, continual

decrease in performance and in some cases with a change in appearance. A coating is considered compatible with a particular liquid if the thickness of the coating changes by no more than 10% on exposure to that liquid.

Table III shows the results of permeability and compatibility tests on polyurea coatings with a variety of petrochemicals. The results indicate that polyurea coatings are impermeable, as defined by most regulatory requirements, to many commonly used petrochemicals. In addition, test results show that they are compatible with these materials after exposure times of greater than one month.

CASE STUDIES: APPLICATIONS OF POLYUREA COATINGS

Following are case studies for four different applications of polyurea coatings in the petrochemical, utility, paint, and chemical industries. These are intended to illustrate the variety of conditions in which polyurea can be applied, and the different substrates on which the coatings can be used.

Case I: A major utility in the California Desert Southwest has a power plant which uses a coal/water slurry as a fuel source. In the late 1970's, eight storage ponds, each about 300 feet in diameter and 50 feet deep were built in order to insure an adequate supply of fuel. The ponds are constructed of asphalt over a sandy soil. The Colorado River runs nearby.

The utility has been under pressure from regulatory bodies to first, reduce the loss of water through cracks in the asphalt, and second, to eliminate the transport of water soluble contaminants through the sandy soil to the river.

To address the problem, the utility chose a polyurea coating. The asphalt surface was cleaned, and the larger cracks filled with asphaltic concrete. A lightweight, spunbonded geotextile fabric was lightly tacked to the asphalt surface of the pond using a 5-10 mil coat of the polyurea as the adhesive. This gave a smooth surface onto which the polyurea topcoat, at an average thickness of 50 mils, was applied. Air temperatures during application ranged from 50° F to over 100°F. Application of the coating to the pond took eleven days. Results ten

months after application indicate that leakage from the pond has been stopped.

Case II: A chemical compounder in Eugene, OR needed an impermeable membrane on a concrete containment area to meet expected future environmental regulations. The area was power washed at 4,000 psi to remove dirt and other surface contaminants. Holes in the concrete walls opened by power washing were patched with an epoxy concrete. Equipment and tanks in the area were masked to prevent possible discoloration from overspray. A polyurea coating was applied to the concrete at 80-125 mils. Application to the 1,200 square foot containment area took about 30 minutes. Two and a half years after installation, the polyurea coating has maintained its integrity even though some new cracks have appeared in the concrete surface.

Case III: A paint company in Eugene, OR wanted to line it's concrete xylene and toluene storage area. On inspection, it was discovered that the concrete on the floor of the containment area had deteriorated badly, and that the cost to repair the concrete would triple the cost of the project.

In this case, a non-woven polypropylene geotextile was cut to fit the area, and placed on the floor and up the wall of the containment area. Each piece of geotextile was overlapped about 4 inches onto the adjacent piece, then glued together using the polyurea coating as an adhesive. The textile was bonded to the top of the concrete wall of the containment area. The polyurea coating was applied at a thickness of 60-125 mils on the geotextile, creating a seamless "bladder" inside the concrete walls. Application of the coating took place in November 1993 at an ambient temperature of 40°F.

Case IV: The owner of a petrochemical storage facility in Houston, TX wanted to coat the concrete tank ring of a gasoline storage tank to prevent water from moving under the tank through cracks in the concrete to cause corrosion. The concrete surface was of excellent strength, and was detergent washed and power washed to clean the surface. Cracks of greater than 1/4" were filled with a polysulfide sealant. The tank ring was then coated with 60-80 mils of polyurea. Temperatures during application ranged from 75°F to 90°F at relative humidities of 50% to 80%. Inspection one year later showed the coating to be performing well, adhering tightly even to those areas where the concrete was saturated with gasoline.

CONCLUSIONS

As environmental regulations continue to change, containment of liquids in storage areas is an issue now, and will certainly be one in the future. Because of the advantages they offer in performance, polyurea coatings are often a good selection for primary and secondary containment applications in the petrochemical industry. These advantages are: (1) The coatings form a seamless barrier, (2) They attach directly to penetrations such as tanks, (3) They are tough, flexible materials which stand up well to traffic, (4) Polyurea coatings offer good performance at low temperatures, (5) They have good stability to UV radiation, (6) They do not expand and contract excessively, (7) They may be applied under adverse environmental conditions, and (8) They offer good chemical resistance to a variety of petrochemicals.

REFERENCES

1. Code of Federal Regulations, Volume 40, No. 112, "Spill Protection, Control, and Countermeasure Regulations."

2. Florida Department of Environmental Protection, Chapter 62-762, "Above Ground Storage Tank Systems."

3. Texaco Chemical Company, "Polyurea Spray Technology Information," Technical Bulletin, 1989.

TABLES

Table I

Typical Physical Properties of Polyurea Coatings

Property	Test Results	Test Method
Tensile Strength, psi, 25° C	3,229	ASTM D 412
Elongation, %, 25° C	418	ASTM D 412
200% Modulus, 25° C	2,712	ASTM D 412
Die C Tear Strength, pli	527	ASTM D 624
Puncture Resistance, lb.	351	ASTM D 4833
Hydrostatic Resistance, psi	526	ASTM D 751
Mandrel Bend, -60° F, 1" mandrel	No cracking	ASTM G 11
QUV Weatherometer, 313 UV bulb, 7,100 hours (19.7 years)	No cracking	ASTM G 53

Table II

Comparison of Polyurea Coatings to Other Common Secondary Containment Liners[1]

		Containment Liner Material			
Property	Polyurea	Epoxy	Polysulfide	HDPE	Polyurethane
Tensile Strength, psi	3,229	2,500	---	---	2,878
Elongation, %	418	5	81	750	52
Puncture Resistance, lb.	351	---	88	70	351
Expansion/Contraction, -5° F to 200° F, %	-0.46-0.15	---	---	2.0-2.2	---
Moisture Sensitive?	No	Yes	---	No	Yes

[1]Physical properties for competitive materials may be measured using different test methods. Where possible, these measurements have been converted to the same units to improve the validity of comparison. Results are not reported when these conversion factors are in doubt.

Table III

Permeability and Compatibility of Polyurea Coatings with Common Petrochemicals

Petrochemical	Permeability, cm/second[1]	Compatibility (% Change in Thickness)[2]
Unleaded Gasoline	3.8×10^{-8}	+10.2
Diesel Fuel	1.2×10^{-8}	+3.1
Kerosene	1.2×10^{-8}	+4.8
Jet A Fuel	7.8×10^{-9}	+1.7
Motor Oil	9.9×10^{-9}	+0.4
Fuel Oil #2	2.9×10^{-9}	+2.0
Water	9.3×10^{-9}	+3.3
Regulatory Standards	Anywhere from 10^{-7} cm/s to 10^{-4} cm/s	

1 ASTM E 96 Test Method

2 Compatibility with petrochemical products is calculated by measuring the sample thickness before and after exposure to the chemical, and calculating the per cent change in the thickness of the coating.

Thermal Remediation and Recycling of Oily Solids Generated in Oil Field Operations

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Abstract:

Generation of oily solids at the Kuparuk River Field on the Arctic North Slope is minimized by an aggressive pollution prevention program. However, some materials are still generated. Fracture and formation sands are the largest volume of oily materials generated; smaller volumes of gravel contaminated by petroleum spill are also produced. Small volumes of non-oily materials are commingled with the oily solids.

Storage of these materials at Kuparuk began in 1989. In 1992 the solids were thermally remediated on-site using a mobile incineration facility. Approximately 11,300 cubic yards (17.910 metric tons) of material was remediated and placed in 76 segregated piles while testing was conducted for hydrocarbons and 12 heavy metals.

Final release was based on a combination of release criteria. All material was subsequently released for reuse and placed as encapsulated fill in a drill site access road. Since this project was completed work has focused on using the information gained in this project to improve the cost-effectiveness of handling oily solids.

Introduction

The Kuparuk River Oil Field, operated by ARCO Alaska, is the second largest oil field in North America. The field is located adjacent to the Beaufort Sea in northern Alaska. The nearest village; which has only 200 residents, is 40 miles to the west. Due to its remote location, facilities include a camp, three production facilities, 42 remote drill sites, a crude oil topping unit, a Sea water Treatment Plant and a small airport. Temperatures range from an average of minus 22 degrees F. in mid-winter to 39 degrees F. in summer.

The land on which the field is developed is underlain by permafrost which limits surface drainage to an active thaw lay of approximately 18 inches. In this dry, cold climate region, water accumulates in small tundra ponds formed by a process known as thermokarsting. Due to the poor surface drainage and the presence of the numerous tundra ponds, all land in the Kuparuk area is classified as wetlands. The wetlands classifications restricts fill activity such as road building. Buildings are placed on pilings and unpaved gravel roads and work pads (drill sites) are constructed to protect the sensitive tundra surface from additional thermokarsting.

At the time this project was initiated there had been no similar remediation projects completed in Alaska. There had been numerous petroleum hydrocarbon remediations associated with leaking storage tanks so state clean-up guidelines existed for petroleum hydrocarbon remediation (1). However, the materials stored in the Kuparuk facility had the potential for metals contamination as well.

At the beginning of the project the chemical composition of input materials was not well defined. Little was known about metals composition of the input materials. Hydrocarbons of concern were heavy paraffins and waxes rather than the crudes and diesels more commonly associated with tank remediations. The challenge of this project was to test the effectiveness of standard thermal remediation (incineration) on these heavy hydrocarbons and to improve project economics.

Background

Oily solids and other solids generated in the course of exploration and production operations are collected and stored. This management approach hinges on periodic remediation of the solids. Batch remediation every five to eight years allows sufficient material to be accumulated to make remediation cost-effective.

In 1989, Kuparuk built the first of two adjacent open pits (cells) to store oily solids temporarily pending remediation or disposal (Fig. 1). A second storage cell with impermeable double liners and a leachate collection system was constructed in 1990. The smaller pit is only used for contingencies. Snow melt and fluids, which separate out when the frozen solids thaw, are collected in two sumps and recycled.

The storage facility is located on an active drill site. A locked gate prevents unauthorized entry and off-loading. During the thaw period a fence surrounds the facility to inhibit terrestrial wildlife entry; the fence is removed in winter to reduce the amount of snow trapped.

A small pilot project to demonstrate the efficiency of the proposed remediation process was successfully completed in the spring of 1992. A mobile thermal soil remediation unit available on the North Slope was permitted by the Alaska Department of Environmental Conservation to remediate exploration and production exempt and non-exempt, non-hazardous oily solids. A firm was contracted to excavate, thermally remediate, and certify hydrocarbon removal. The incinerator had an operating efficiency rate of 79%; downtime was used for plant inspection, maintenance, calibration and repairs.

In August 1992 more than 11,300 cubic yards (17,910 metric tons) of solids were thermally remediated and reused as road maintenance material. Since this was a pilot project, Kuparuk restricted placement of remediated gravel to existing roads and pads to alleviate concerns regarding placing previously contaminated materials on virgin tundra. Based on the successful 1992 remediation, additional gravel disposition such as new pad construction will be considered for future remediation projects.

Stored Material Characterization

Stored solids are primarily generated in oil production activities and contaminated with process fluids. Materials fall into three primary categories: spill residues, materials brought to surface in oil production activities, and maintenance solids (Table 1).

Spill residues are tracked separately since they typically have a large volume and a low petroleum hydrocarbon content. This category consists of road and pad gravel contaminated with small amounts of petroleum hydrocarbons. In the past it was common practice for all spills to be cleaned up with heavy equipment; this practice resulted in large volumes of clean gravels being commingled with smaller amounts of contaminated gravels. Current practice is to limit picking up clean gravel by only using heavy equipment when necessary.

Formation solids are contaminated with crude, diesel, produced water, stimulation acids and low concentrations of process chemicals such as corrosion inhibitors, emulsion breakers, and scale inhibitors. As oil is produced, solids are dislodged from source rock and brought to the surface where they settle out in pipelines, vessels and tanks. Solids are also flowed back to the surface during well work. Formation solids are both rock particles and man-made proppants injected into the source rock to cause fractures which allow more oil to be recovered.

Other miscellaneous solids such as contaminated tundra mat, sandblast sand and garnet or anthracite filter media are also stored in the solids storage facility.

Reuse Criteria

Since this was the first project of its type in Alaska, it was necessary to develop appropriate remediation criteria. A combination of three criteria were applied to the project: a hydrocarbon release criterion, a metals release criterion and a toxicity release criterion. The remediated material had to meet all three criteria to be reused. Material recycling was dependent on meeting all three criteria.

The petroleum hydrocarbon remediation criterion was an established clean-up standard developed for leaking storage tank remediations (1). The interim metals release criterion was developed for a drill cuttings reuse project (2). The heavy metals criteria were based on an analytical protocol that allowed screening for total metals concentration; the total metals concentration was determined by an acid extraction method which reduced sampling costs and projects delays.

If the materials meet the total metals screening (i.e. primary) release criterion, then the more costly, leachable metal analysis was avoided. A water extraction method was used to determine leachable metals. The toxicity criterion was based on the hazardous waste toxicity leaching procedure. The combined interim release criteria are summarized in Table 2.

Gravel and formation sands contain naturally-occurring metals. Criteria based on 90% of mean background levels for North Slope soils and gravel were selected. These standards had been established for a drill cuttings reclamation pilot project in which surface hole drill cuttings were washed and reused.

Naturally occurring radioactive materials (NORM) can be produced when scale forms from subsurface produced waters. Background NORM for Kuparuk is 0.03 mRem/hr. NORM readings were taken at the storage facility and from tanks at each of the Central Production Facilities. All readings were less than background so NORM testing was not required on the remediated material.

1992 Remediation

The 1992 remediation work consisted of the following activities: thermal remediation (incineration), analyzing representative samples for reuse criteria, storing processed solids pending receipt of data, and recycling the material. The incinerator was located near the storage facility (Fig. 1). Oily solids were excavated with a bulldozer and loader. A rock crusher sized material for optimal incinerator efficiency. Containment liners were installed to prevent pad contamination during the remediation process.

The incinerator consisted of two stages. In the first stage solids were heated to 600°F-800°F to vaporize hydrocarbons. Then vapors were oxidized in the second stage at 1600°F. Fine particulates generated in the first stage were captured in a bag house, re-mixed with coarse solids, and water-quenched prior to discharge. These finer particles enhanced the binding properties of the gravel, improving its quality for construction and maintenance purposes.

Remediated material was stockpiled directly on the pad pending analytical results (Fig. 1). Hydrocarbon samples taken for each 100 cubic yards of material were

composited at 25 cubic yard intervals. One batch exceeded the petroleum release criteria and was re-processed. Composites were taken every 400 cubic yards for toxicity characteristics. Five-point composite metals samples were taken for each of the 76 stockpiles.

Metals in soils and gravels are associated with finer particle sizes. Standard analytical procedures dictate small analysis weights; therefore, only fine particulates are digested and resulting metals concentrations are biased. Sieve analysis of seven samples showed the remediated material to have a uniform size distribution. Analytical results were corrected for the analytical bias (3, 4).

Average metal concentrations were used to determine material recyclability because data from thermally treated material showed little variation in metal concentration between samples (Table 3). The sieve analysis discussed earlier showed that the material was very uniform in size. Incineration was effective destroying the heavy hydrocarbons. The metals content of the mixed solids was similar to background. Therefore, one might conclude that the release criterion could be simplified in future remediations. The number of metals analyzed should be reduced to target the six metals for which the mean concentrations approach background.

Table 3 shows that the strict release criteria were met for all but one element; the average lead concentration exceeded the release criteria by 30 percent (16.9 mg/kg vs. 11.8 mg/kg). During the six months between when the release criteria were developed and remediation was initiated it was decided that release criteria based on 90% of mean background were more conservative than necessary.

A review of pertinent literature revealed that risk-based release criteria of 250-1,000 mg/kg lead were commonly found in other remediations (5). Additionally, the review indicated that background lead levels in Arctic lake sediments were approximately 20 mg/kg which was 10-20 percent greater than the average for the remediated material (6) . The remediated material was approved for release and was used for road maintenance.

Waste Minimization and Alternative Technologies

Once the materials in the storage facility had been remediated, it was possible to review the analytical data and develop a plan to change the way solids are managed and thereby reducing future remediation costs. An effective approach to minimizing solids management costs is to reduce the amount of solids generated. The Kuparuk River Unit has an aggressive waste minimization program which stresses reducing or eliminating waste whenever possible. Periodic opportunity assessments are performed to identify potential waste reduction activities.

A number of pollution prevention activities have been implemented since the 1992 remediation project was completed which should reduce the metals content of the material stored in the storage facility. Leaded pipe dope was replaced with a non-leaded brand to reduce lead contamination on oily solids generated in drilling or well work. The volume of fluids spilled annually is much less than one percent of the total volume of fluids handled each year. However, there is an on-going focus to reduce the number and volume of spills. Concurrently, efforts have focused on reducing the amount of excess clean gravel removed during clean-up.

Other projects are under evaluation. Materials brought to the surface in drilling and production operations may be injected directly into Class II disposal wells rather than being stored in the solids facility. This is the current handling practice for drill cuttings from exploration wells; the practice could be expanded to include formation sands and vessel sediments. An evaluation of transportation, injection facility and handling costs is currently underway. Direct re-injection of these materials would significantly reduce the annual volume of materials stored, thereby increased the amount of time between batch remediations.

Miscellaneous small waste streams that have been put into the storage cell in the past have been evaluated and diverted to other immediate handling or reuse options. Used sandblast sand is tested for metals concentration; when it meets primary release criteria it is used to fill sand bags. Sandblast sand can also be used as a finish grading layer under lined secondary containment areas. Tundra mat and other organic residues are incinerated with paper trash at the time they are generated.

Additional technological alternatives to thermal remediation are currently under consideration. These include bioremediation, washing and bio-slurry techniques. Due to the harsh Arctic climate and Kuparuk's remote location, these options present unique technological challenges, but may replace thermal remediation

Conclusions and Recommendations

Waste minimization is a cost-effect management practice for oily solids. However, at this time, it is not possible to directly reuse or recycle all oily solids. Incineration and subsequent recycling proved to be a successful management practice which can be used in environmentally sensitive environments such as North Slope tundra ecosystems.

Information learned in the 1992 project can provide the basis for fine-tuning release criteria in future remediations. Materials generated since the 1992 remediation are generally similar in type and relative proportions. Therefore, the metal, hydrocarbon, and toxicity composition of the presently stored material is expected to be similar to that processed in 1992.

Traditional petroleum hydrocarbon thermal remediation techniques successfully remediated the crude and heavy paraffin contaminants associated with formation sands and vessel sediments. Metals data collected during this project suggest that simplifying the metals release criteria is warranted. Sufficient data now exist to show that reducing the number of metals in the combined criteria to include only arsenic, barium, cadmium, copper, lead and zinc would still adequately protect the environment. Future release criteria for these six metals should incorporate risk-based information which has become available since the 1992 criteria were established.

References

(1) Alaska Department of Environmental Conservation, Interim Guidance for Non-UST Soil Cleanup Levels, July 17, 1991.

(2) Primary Interim Release Criteria established as part of Phase II of NS Drill Cuttings Reclamation Project approved by the Alaska Department of Environmental Conservation, February 2, 1991.

(3) Federal Register, Vol. 55, No., 61, Sections 8.13.2 and 8.14.

(4) Bowman, G. T., 1992. Weight Adjustment Based on the Contribution of Inert Materials. Memorandum.

(5) New Jersey Clean-up Responsibility Act, 1987.

(6) Huang, P. M., and W. K. K. Liaw, 1978. Distribution and Fractionation of arsenic in selected fresh water lake sediments. Internationale Revue der Gasamten Hydrobiologie 63:533-543

Table 1: Material Composition

Material	Composition
Materials brought to surface in oil and gas exploration and production activities	62%
Spill Residues	29%
Miscellaneous solids	9%

Table 2A: Release Criteria - Metals

Element	Primary Interim Release Criteria[1] (mg/kg)	Secondary Interim Release Criteria[2] (mg/kg)
Aluminum	16324	12.29
Arsenic	5.0	.00456
Barium	1600	.383
Cadmium	.44	ND
Chloride	4925	
Chromium	35.0	ND
Copper	31.8	.ND
Lead	11.8	.00255
Mercury	.71	ND
Nickel	43.6	ND
Selenium	.56	.00117
Silver	.52	ND
Sodium	1537	17.73
Sulfate	2251	
Zinc	144	.0984
ND = Not Detected		

Table 2B: Release Criteria - Hydrocarbons

Parameter	Interim Reuse Criteria (mg/kg)	Method
TPH	200	418.1
Benzene	0.5	8020
BTEX	10	8020
TCLP Benzene	0.5	1311/8020

1 Primary Interim Release Criteria established as part of Phase II of NS Drill Cuttings Reclamation Project approved by the Alaska Department of Environmental Conservation, February 2, 1991.

2 Secondary Interim Release Criteria established as part of Phase II of NS Drill Cuttings Reclamation Project approved by the Alaska Department of Environmental Conservation, February 2, 1991.

Table 3: Results - Primary Metal Criteria

Metal	Criteria	Maximum	Average	Std. Dev.
Aluminum	16324	3198	2092	421
Arsenic	5.00	12.02	4.70	1.99
Barium	1600	1207	603	207
Cadmium	0.44	0.26	0.13	0.03
Copper	31.8	31.2	19.2	4.2
Chromium	35.0	16.1	9.1	2.4
Lead	11.8	28.4	16.9	5.1
Nickel	43.6	17.1	10.0	2.1
Mercury	0.71	<0.15	NA	NA
Selenium	0.56	0.30	0.18	0.05
Silver	0.52	0.08	0.07	0.004
Zinc	144.0	223.8	45.3	23.3

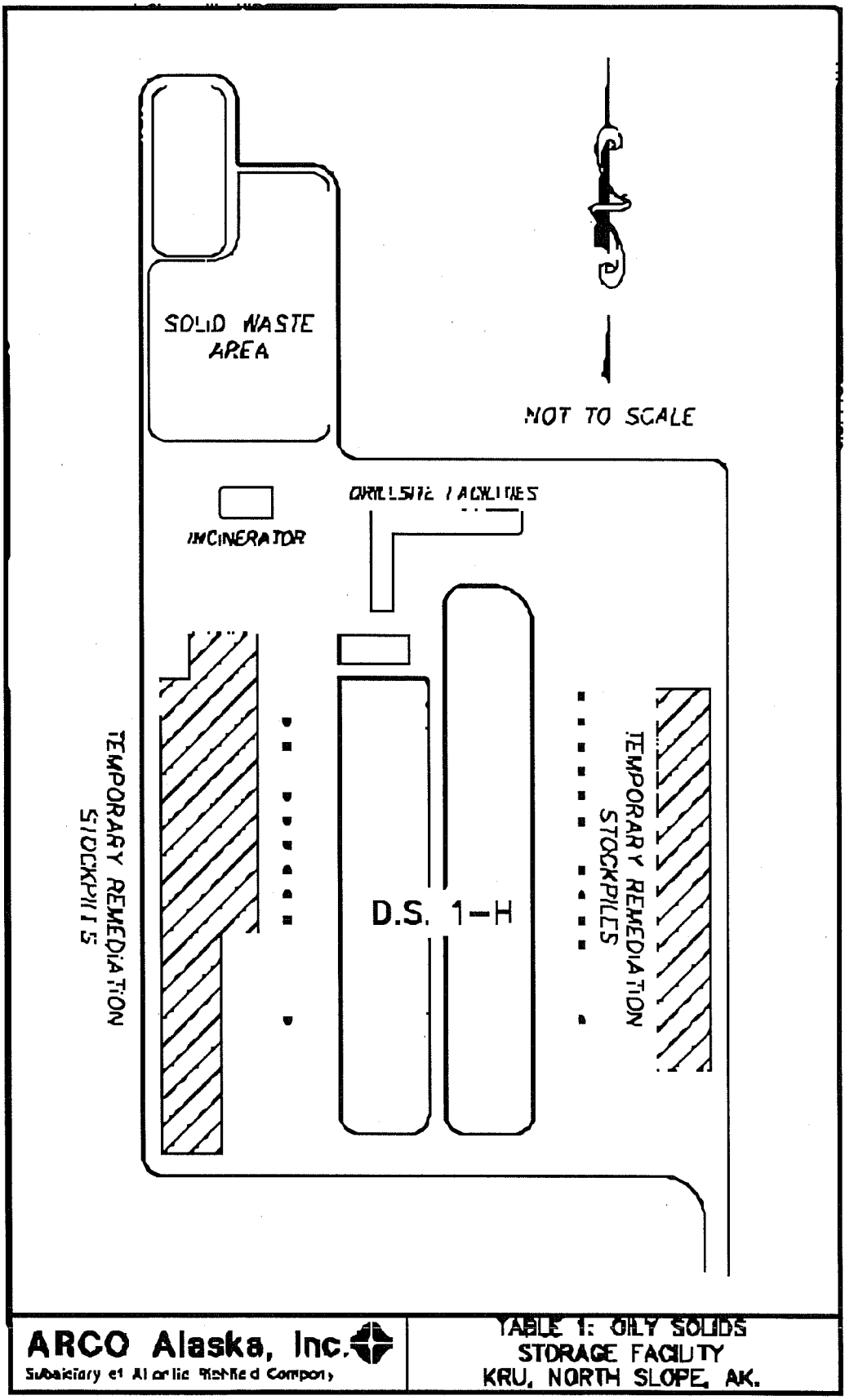
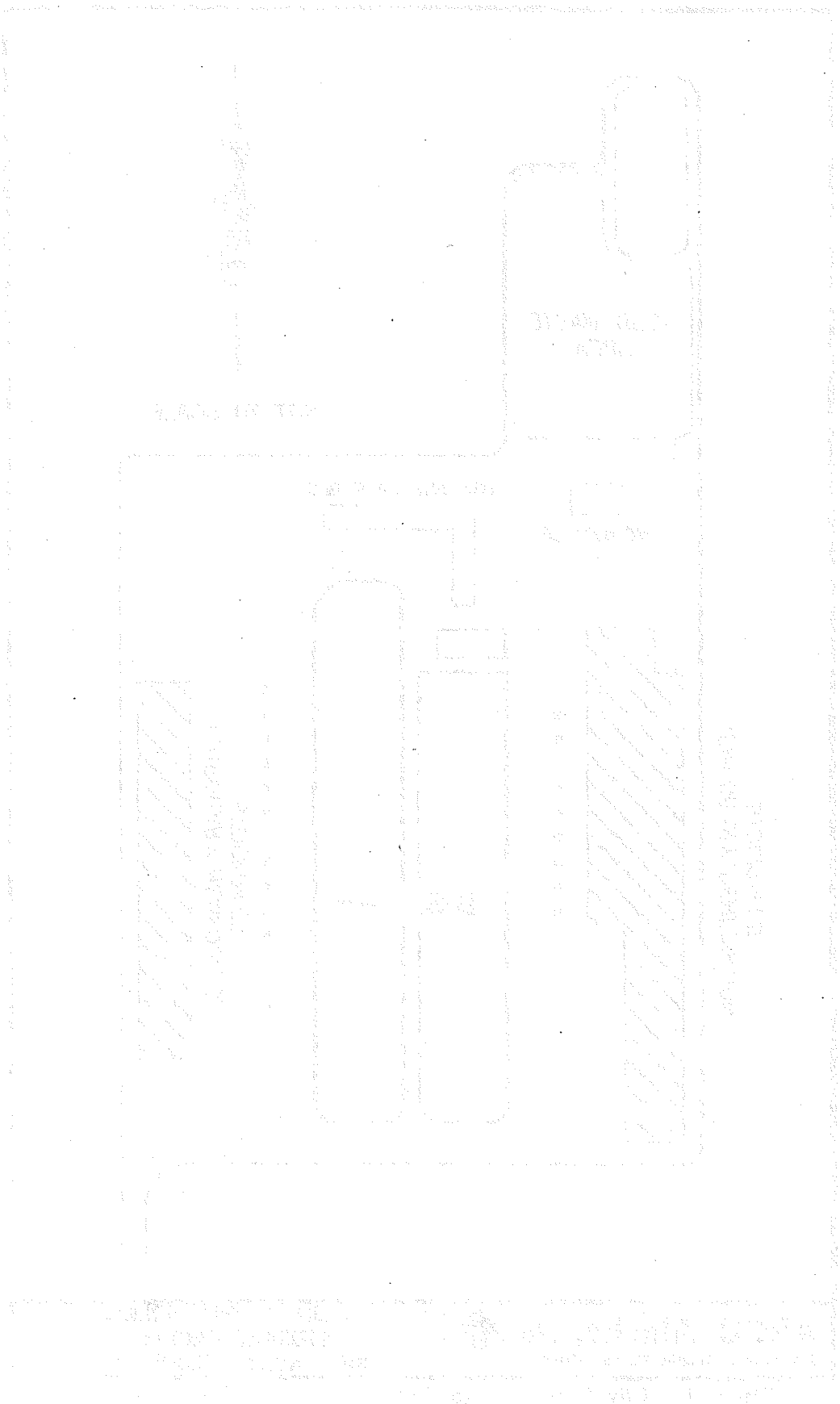


Figure 1: Oily Solids Storage Facility, Kuparuk River Unit



Considerations For Acid Gas Injection

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ABSTRACT

When sour gas is sweetened by a regenerable solvent such as amine, hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are removed from the hydrocarbon gas stream. Normally these gases are further treated in a sulfur recovery process. The unrecovered sulfur is subsequently converted to sulfur dioxide (SO_2) and disposed of into the atmosphere with the CO_2. As an alternative, the compression and injection of acid gas mixtures of H_2S and CO_2 into an underground zone is an environmentally preferred solution for disposing of these compounds. Under certain conditions, this solution is also more economical than the sulfur recovery options. This paper discusses the properties of compressed, water saturated acid gas mixtures, and reviews the considerations that have to be addressed in the design and operation of acid gas injection facilities. Cost comparisons between acid gas injection and some sulfur recovery options are presented for Canada, and areas of research to further enhance the economic advantages of acid gas injection are indicated.

INTRODUCTION

Natural gas is a mixture of light hydrocarbon gases, consisting mainly of methane and minor quantities of other heavier compounds such as ethane, propane, butane, etc. Some non-hydrocarbon compounds are also usually present in natural gas, such as nitrogen, helium and carbon dioxide (CO_2). When the gas contains hydrogen sulfide (H_2S) in concentrations above a few parts per million by volume, the natural gas is said to be "sour". All sour gas has to be treated for the removal of virtually all of the H_2S before it can be sold commercially. The separation of the H_2S from the natural gas is usually accomplished by contacting the sour gas with a solvent, which absorbs the H_2S. All sour natural gases

contain some CO_2, which is also extracted with the H_2S by the solvent. The H_2S and CO_2 are usually called "acid gases", since they are slightly soluble in water, producing a mildly acidic solution. The process by which the acid gases are extracted from the sour natural gas is called "sweetening".

Upon the separation of the acid gases from the sour natural gas, the acid gas stream is usually treated for the recovery of most of the sulfur in the H_2S. The unrecovered sulfur is converted to sulfur dioxide, and is vented to the atmosphere, along with the CO_2, in highly diluted concentration through tall stacks and at high temperatures. These gases are then dispersed in the atmosphere, resulting in very low concentrations at ground level.

The sulfur recovery processes require major equipment installations, at substantial capital cost. They are also expensive to operate, and generally at present the sulfur product does not recover all of such costs. Hence there is not much incentive to recover the sulfur for its economic value. The choice that the operating company then has to make is which process to use to handle the acid gas at the lowest cost, and to comply with the environmental regulations. The most common choices of processes for sulfur recovery are:

- modified Claus process,
- direct oxidation process,
- LO-CAT II®[a] process,
- SulFerox®[b] process.

The quantity and composition of acid gas to be handled will have the greatest influence regarding the selection of the method for disposing of the sulfur contained in the H_2S from the sour gas. The injection of the acid gas into an underground disposal zone is discussed in this paper. This method may be more economical than other methods under certain conditions, and has the advantage of not venting acid gases to the atmosphere. While compression and injection is environmentally the preferred method of disposing of the acid gases, there are certain considerations that must be taken into account:

- technical considerations,
- regulatory considerations,
- economic considerations.

TECHNICAL CONSIDERATIONS

In the design of acid gas compression and injection facilities, it is very important to understand the physical behavior of the acid gas mixtures at elevated

[a] LO-CAT II® is a registered trademark of Wheelabrator Clean Air Systems, Inc.
[b] SulFerox® is a registered service mark of Shell Oil Company.

pressures, as well as the interaction between water and the acid gas components in both their vapor and liquid states. While experimental data for acid gas mixtures do not appear to be available in the published literature, the behavior of pure H_2S and pure CO_2 with water has been extensively studied and the results have been published.

1. Physical Properties

Figure 1 shows the pressure-temperature profiles for the individual acid gas compounds, namely H_2S (1) and CO_2 (2), as well as for methane (CH_4) (2), in solid lines. To the right side of each line, each compound is in the vapor state. At the temperature and pressure on the line, each compound will exist in both the vapor and the liquid states. To the left of each respective line, the compound will exist in the liquid state. At the pressures and temperatures above the top of each line, each compound exists in a dense phase, which is neither a liquid nor a vapor. Also shown in Figure 1 are two dashed lines, which represent the hydrate forming lines for H_2S (3) and CO_2 (4). The hydrate line for CH_4 is close to the hydrate line for CO_2, and is not shown.

Figure 2 shows the behavior of the water content at saturation for pure H_2S (3) and pure CO_2 (5), at various temperatures. Also shown in Figure 2 is the water content of a mixture of 94.69 % CO_2 and 5.31 % CH_4 (6), showing that the small amount of CH_4 has a marked influence in lowering the water content at saturation of this particular mixture at elevated pressure. The water content of hydrocarbon gases decreases with increasing pressure, at a given temperature. It is evident from the lines in Figure 2 that for the acid gases, there is a reversal of this trend, namely, at certain elevated pressures the equilibrium water content actually increases with pressure. Thus for any given temperature, there is a pressure at which the saturated water content in the acid gas is at a minimum. In acid gas compression and injection, this behavior is significant, as it may obviate the need to dehydrate the acid gas mixture.

When the acid gases are removed from the raw sour gas stream, the resulting acid gas mixture contains H_2S, CO_2, minor amounts of CH_4 and is saturated with water vapor. The pressure of this mixture at that point is generally in the order of 70 to 100 kPa gauge (10 to 14.5 psig), and the temperature is in the order of 25 to 40 °C (77 to 104 °F). These conditions will vary somewhat among the various sour gas plants, and also with the ambient temperatures available for cooling the regenerator overhead stream. This is the mixture that is further treated for sulfur recovery, or is compressed and injected into an underground disposal zone.

Hydrates are solid compounds that form with free water with certain gases, such as the acid gases and CH_4, at elevated pressures. Figure 3 shows the

hydrate forming temperature, as generated by a software program called HYSIM™ (7), for acid gas mixtures containing various H_2S concentrations, with the balance being 1 % CH_4 and the rest CO_2. As can be seen, the hydrate temperatures increase with increasing content of H_2S in the acid gas mixture. Hydrates of course will not form if there is no liquid water phase present.

Any gas can be liquefied if it is sufficiently cooled. When the acid gases exist in mixtures, a two-phase region is established between the lines shown in Figure 1. Such two-phase envelopes are shown in Figure 4 for acid gas mixtures containing 1 % CH_4 and the balance being 10 % H_2S and 89 % CO_2 as well as a mixture of 50 % H_2S and 49 % CO_2, as generated by HYSIM™. As can be seen, the two-phase envelopes are very narrow in temperature range, and also that the mixtures will exist in the liquid phase if the temperature is below 20 °C (68 °F) at a pressure of 6000 kPa (870 psi) or higher. This means that acid gas mixtures at elevated pressures are readily liquefied by aerial cooling. If the acid gas mixture contains considerable amounts of light hydrocarbon gas, then the two-phase envelope for the mixture becomes wider in temperature, as illustrated in the third envelope in Figure 4, which contains 10 % CH_4 and 45 % each of H_2S and CO_2.

2. Problem Areas

From the foregoing, it is evident that during compression and injection of acid gas, the possibility exists that hydrates could form and that a liquid phase of the acid gases can also form. Additionally, the combination of acid gases, free water from condensation and high pressure and temperature are the ingredients for potential corrosion problems in carbon steel pipes and vessels. The design engineer and operating personnel must understand the conditions under which these undesirable factors can occur, and design and operate the facilities to prevent such occurrences.

Both of the problems, namely hydrate formation and corrosion, will occur only if there is a liquid water phase present. Hydrates can be prevented by operating above the hydrate forming temperatures at operating pressures as shown in Figure 3, or by adding a chemical inhibitor such as methanol to lower the hydrate forming temperature. Corrosion can be handled by using stainless steel in certain parts of the equipment.

Another method of preventing both problems is to dehydrate the acid gas stream usually after the second or third stage of compression. This, however, adds another process into the overall compression and injection scheme, adding to both the capital and operating cost.

Whether or not acid gas dehydration is necessary is debatable. After the

third stage of compression the pressure would generally be in the range of 2000 to 4000 kPa (290 to 580 psi). This is the approximate pressure range at which the acid gas mixtures exhibit the minimum water content at saturation, as indicated in Figure 2. By cooling the gas to within two to five degrees of the hydrate temperature shown in Figure 3 after the third stage of compression, the minimum water content in the gas mixture is generally achieved. Upon compression after the fourth stage and cooling to near ambient temperatures, the acid gas is generally in the liquid phase or the dense phase as discussed previously and as illustrated in Figure 5. At the final pressure, the acid gas mixture can hold a lot more water in solution than after the third stage of compression. As a result, there should be no water condensing at the maximum injection pressure, and the above mentioned problems of hydrate formation and corrosion should not occur. It is assumed that the hydrocarbon content of the acid gas mixture will be low, normally less than two to three percent.

The above described behavior of water content in acid gas mixtures is inferred from experimental data for pure acid gases, such as presented in Figure 2. Research is required in this area to better define the limits of water of saturation at operating pressures and temperatures, in both the liquid and vapor states of acid gas mixtures, as well as in the dense phase. If methanol is to be used for hydrate suppression, knowledge of the methanol content at saturation in acid gas mixtures would also greatly help the design engineers and operators of acid gas injection facilities.

3. Acid Gas Compression

The ultimate pressure to which the acid gas has to be compressed depends on the pressure of the reservoir, the permeability of the injection zone, and the depth of the zone. If the acid gas mixture is compressed to about 6000 kPa and cooled below 20 °C, the mixture will be in the liquid phase, provided the methane content is no greater than two or three percent. The density of a liquid acid gas mixture will be in the order of 70 to 80 % of the density of water. Thus the injection pressure into the reservoir will be aided by the density of the acid gas in the liquid state. Depending on the sour gas rate and its acid gas content, the injection rate will generally be low. Many disposal zones have a lower pressure than the hydrostatic head of water. Thus the wellhead injection pressure could be in the order of 6000 to 9000 kPa (870 to 1305 psi), but would depend largely on the injectivity of the reservoir as well as reservoir pressure and depth. The pressure of 6000 to 9000 kPa can be achieved by a four-stage compressor. The total horsepower requirement is generally about 7.94 kW per $10^3 m^3/d$ (300 HP per MMscf/d). Since the acid gas components have similar properties, the composition can vary greatly without affecting the operation of the compressor. This kind of flexibility is not easily handled by the sulfur recovery processes. By including a variable speed drive, considerable variations in throughput can also be handled, which is again an advantage over some other processes.

If dehydration is installed, the equipment would be a normal glycol unit, with a minimum of six trays, using triethylene glycol. In sales gas dehydration, the water content has to be reduced to about 65 mg/m^3 (4 lbs/MMscf). Since the objective in acid gas dehydration is simply the avoidance of a liquid water phase, the amount of water left in the acid gas can be substantially higher than 65 mg/m^3. Thus the dehydration facilities for acid gas could be operated more economically than they would for sales gas dehydration.

One of the problems with dehydration of gas in general and with acid gas in particular is the disposal of the reboiler offgases. There is considerable environmental concern with emitting these offgases to the air. In acid gas dehydration, these offgases have to be collected and incinerated or cooled and recompressed into the acid gas stream.

4. Surface Injection Facilities

The acid gas injection facilities beyond the final stage of compression and cooling consist of an injection line, wellsite facilities and the injection well.

Selection of the type of pipeline material for the acid gas injection line between the plant and the injection well is generally related to whether or not the acid gas has been dehydrated. For dehydrated gas, carbon steel materials meeting sour service specifications can be used. The addition of corrosion inhibitor should be considered. Another pipeline material can be 316L stainless steel. One of the key considerations is the length of the line. Stainless steel is more expensive, and if the cost of the line exceeds the cost of a dehydration unit, then it may be more economical to dehydrate the acid gas stream. The proposed pipeline should be fully evaluated with the vendor of the materials to ensure full compatibility with anticipated process conditions of pressure, temperature and acid gas composition.

The line diameter should be sized for liquid phase fluids if the acid gas mixture contains no more than about two or three percent hydrocarbons. This means that the injection rates would be quite low in terms of liquid quantities. An injection rate of 28 10^3m^3/d (1 MMscf/d) of CO_2 reduces to 44.5 litres/min (11.8 US gal/min) in the liquid phase. Thus the pressure drop in a short, 50 mm (2 inch) diameter line would be quite small, as even 280 10^3m^3/d (10 MMscf/d) would amount to only about 445 litres/min (2.8 Bbls/min) of liquid injection.

At the wellsite, the facilities would be very simple. The wellhead would be equipped with a check valve as well as an emergency shut-down (ESD) valve, and could also incorporate instruments to indicate or transmit to a SCADA system the temperature and pressure at the wellhead.

5. Injection Well

When an acid gas disposal scheme by downhole injection is considered, one of the first questions that arises is whether there is a suitable injection well within a reasonable distance, and the second question is whether the regulatory authority will permit injection of the acid gas into the particular zone that the well is completed in.

The ideal acid gas injection well would be a deep well drilled for this purpose within 200 m of the plant perimeter. The drilling and completion costs are largely dependent on the depth of the horizon. The tubular strings would have to meet sour gas specifications. The completion would include a downhole ESD valve, for safety reasons in case of surface equipment failure. The casing would be protected by a downhole packer and a non-corrosive fluid, such as diesel fuel containing corrosion inhibitor, in the annulus between the casing and tubing, as is normally required for water injection or disposal wells.

REGULATORY CONSIDERATIONS

While the injection of acid gas into an underground disposal zone is environmentally benign, regulators have to address certain considerations with respect to the underground impact that injection may create. The injection horizon must be of sufficient depth so that there is no chance of contamination of fresh water zones.

One type of disposal horizon is the zone that contains oil or gas and that has basically been commercially depleted, or perhaps is still on production. Generally this type of zone has been studied by reservoir engineers and geologists, and the formation pressure and extent of the zone are fairly well established. Sometimes the acid gas could perhaps aid in the recovery of oil, by being miscible with the oil. It would of course be best if the fluids in the zone were sour to begin with, as in that case the central treating facilities could handle the acid gases should they be reproduced.

Another type of injection horizon for acid gas could be a deep zone that contains salt water, and gas would simply be added to the salt water. This type of zone has the advantage that the acid gas disposal well could be drilled near the plant site, thereby minimizing the length of the injection line. While some of the acid gas would go into solution, eventually a gas cap would be established. The concern then would be the potential updip migration of the acid gas. It would be necessary for the engineers and geologists to have a good understanding of such water bearing horizons, their areal extent, pressure limitation, competence of the caprock, as well as adjoining mineral rights ownership.

ECONOMIC CONSIDERATIONS

The price of sulfur fluctuates greatly with supply and demand. The supply of sulfur is provided from four main sources:

- mined sulfur,
- sulfur recovered from sour crude oil in refineries,
- sulfur recovered in upgrading of bitumen in tar sands mining,
- sulfur recovered from sweetening of sour natural gas.

In Canada, the supply of sulfur is mainly from the western part of the country, from sour natural gas. The acid gases are separated by solvents, and the sulfur contained in H_2S is converted to elemental sulphur in about 55 plants, mainly by the modified Claus process. This yields about 6 million tons per year of high quality sulfur, which has to be marketed worldwide. Since the transportation costs to world markets are very high, the value of sulfur at the plant gate is usually very low, or, as is currently the case, it has a negative value.

If liquid processes, such as the LO-CAT II® or SulFerox® processes, are used to recover the sulfur from H_2S, the resulting product does not meet the stringent specifications for commercial sulfur, adding to the cost due to extensive further treatment or disposal of the sulfur in an approved landfill site.

A cost comparison is provided in Table 1 for the various options for dealing with the sulfur recovery or disposal problem. These costs are expressed in terms of Canadian dollars, where $ C 1.00 equals $ US 0.73. In this example, the cost includes the sweetening facilities and the various sulphur recovery facilities for a sour gas plant designed to treat 500 $10^3m^3/d$ (17.75 MMscf/d) of gas containing 2.0 % CO_2 and 0.44 % H_2S.

The total sulphur content in the inlet gas stream in the example is 2.98 t/d. The acid gas stream will contain 18 % H_2S, unless some CO_2 is left in the sweet gas by the chosen solvent. For the purpose of this example it is assumed that all of the CO_2 will be extracted. The capital cost estimate for the equipment, without installation in the field, is shown in Table 1. The capital cost in such installations changes with total sour gas treating capacity and the acid gas content of the sour gas.

Operating cost estimates for all processes are given in Table 2 and include the following items:

- utilities (electricity, fuel gas, water),
- chemicals (catalyst, chelates, iron oxide ions, pH control, corrosion inhibitor),
- maintenance,
- operator time.

The economics of acid gas compression and injection will of course depend also on other factors, such as environmental limitations on sulfur compound emissions, CO_2 emissions, availability of a disposal zone in the vicinity of the sour gas plant, as well as regulator acceptance of the concept of injecting the acid gas into an underground zone.

CANADIAN EXPERIENCE

The first Canadian acid gas compression and injection scheme was installed by Chevron Canada Resources in 1989. Since then, six more schemes have been placed in operation by various companies, and several other proposed schemes have received regulatory approval. Most of these projects will be operational by the end of 1996.

CONCLUSION

The compression and injection of acid gas into an underground disposal zone is environmentally preferred and technically feasible. This method of handling the acid gas stream also provides great flexibility in accommodating changes in rate as well as acid gas composition.

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7. HYSIM™ is a Trademark of Hyprotech Ltd., Calgary, Alberta, Canada

Table 1

Estimate of capital cost of various sulphur recovery processes
(Thousands of dollars)

Process Equipment	Two-stage Claus	One-stage Dir. Oxid.	LO-CAT II®	SulFerox®	Acid Gas Injection
Sweetening	650.	650.	650.	250.	650.
Sulphur recovery:					
Facilities	1,000.	1,000.	2,400.	1,800.	
Catalyst	6.	40.	-	-	-
S Filter/Melt.	-	-	300.	300.	-
Solvent	75.	75.	300.	300.	-
Incin./Stack	150.	150.	-	-	-
Acid gas injection:					
Acid gas compr.	-	-	-	-	650.
Acid gas line(316SS)					40.
Injection well					700.
Royalties	-	100.	150.	200.	-
Estimated Total	1,881.	2,015.	3,800.	2,850.	2,040.

Note: Estimated capital costs are for skid mounted equipment f.o.b. Calgary shop.

Table 2

Estimate of annual operating cost
of various sulphur recovery processes
(Thousands of dollars)

Cost Item	Two-stage Claus	One-stage Dir. Oxid.	LO-CAT II®	SulFerox®	Acid Gas Injection
Electr.Power	76.	95.	78.	104.	153.
Fuel gas	75.	75.	75.	-	75.
Catalyst	2.	13.	-	-	-
Chemicals	25.	25.	320.	350.	25.
Labor,Op/Mnt	150.	150.	250.	250.	200.
Sulphur Disp.	-	-	50.	50.	-
Estimated Total	328.	358.	773.	754.	453.
$ per tonne of S	301.	330.	711.	693.	416.

Assumptions going into these cost estimates:

Catalyst change-out: once per 3 years
Electricity: 10 c/kWh
Fuel gas: $1.50/GJ
Chemicals: routine consumption.

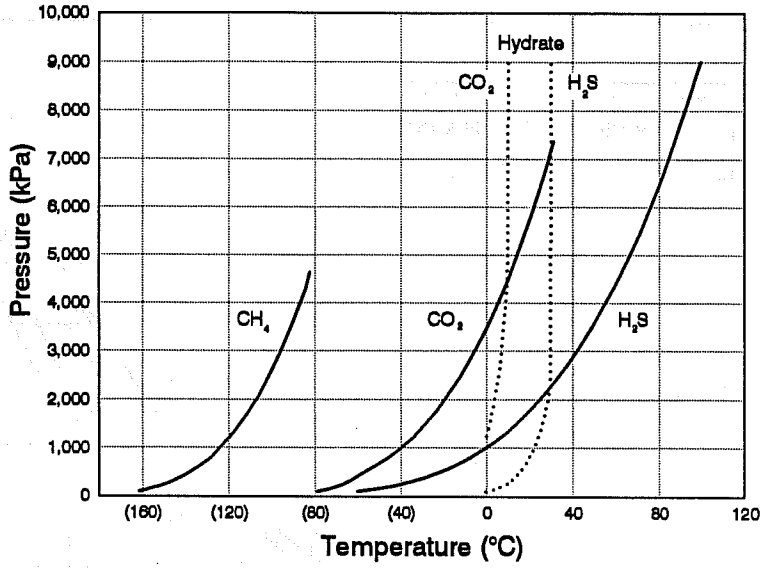

Figure 1. Vapor pressure versus temperature and hydrate conditions for CO_2 and H_2S.

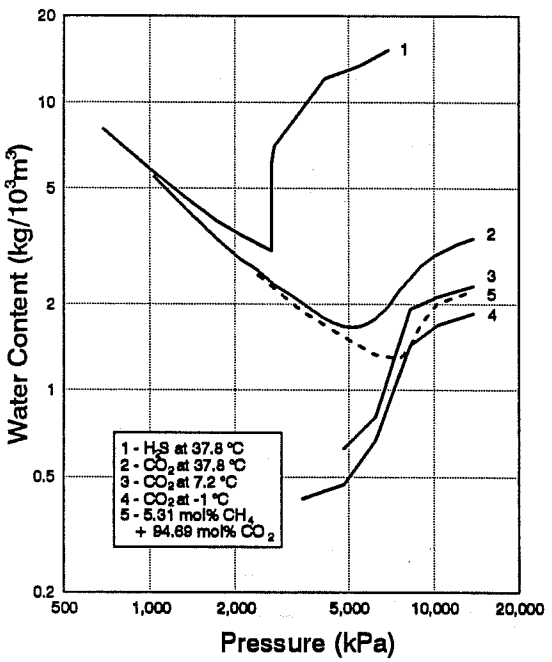

Figure 2. Water content versus pressure.

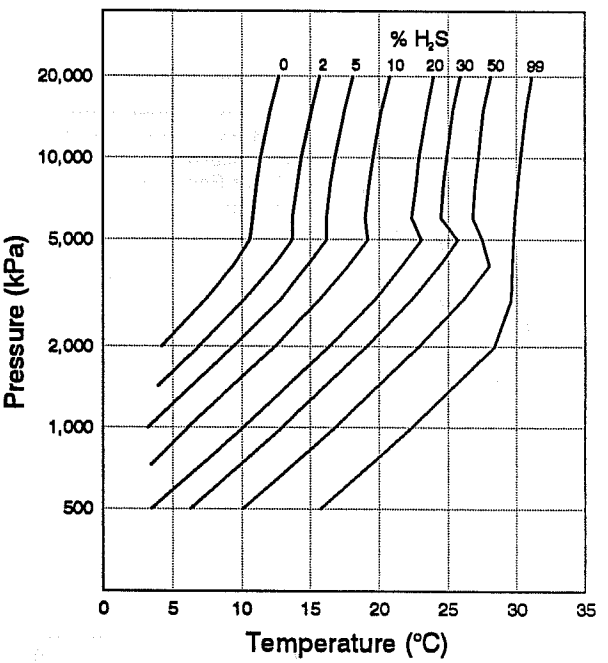

Figure 3. Hydrate temperature versus pressure for acid gas mixtures containing 1 % CH_4, CO_2, and H_2S.

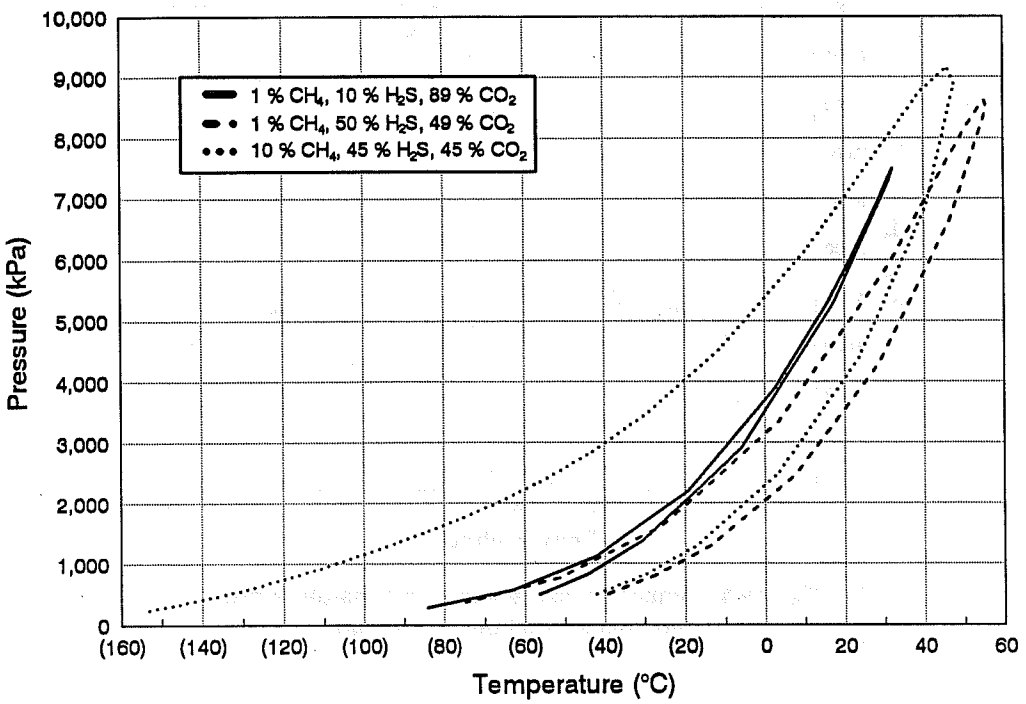

Figure 4. Pressure - Temperature phase envelopes for various gas mixtures.

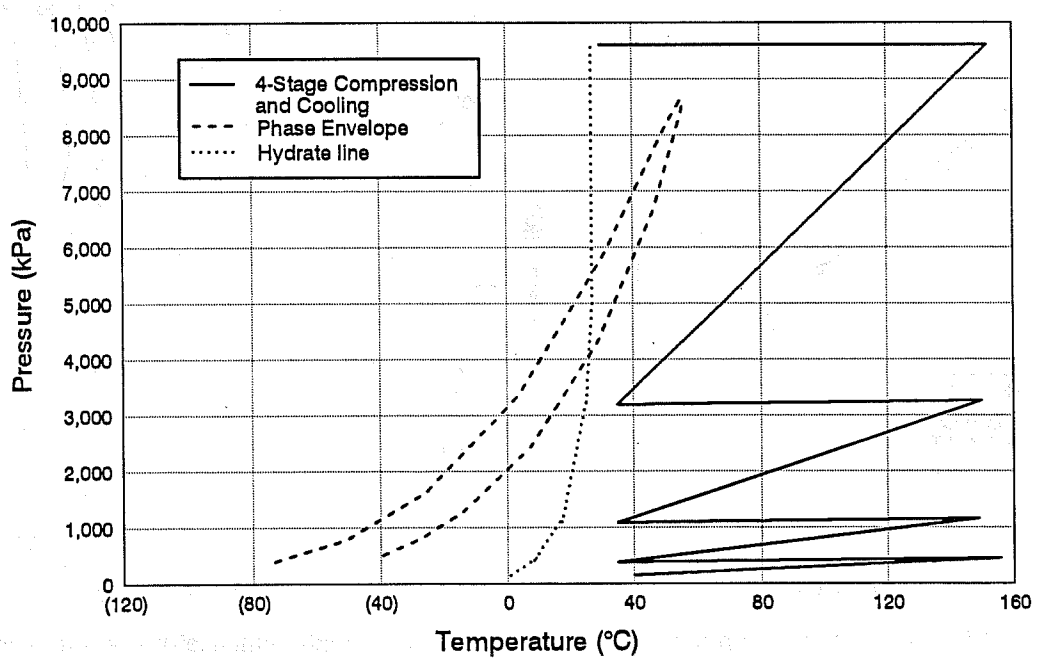

Figure 5. Four-stage acid gas compression showing pressure rise and temperature variations.

Prediction of Vapor Pressures of Refrigerants Using the SVRC Correlating Framework

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ABSTRACT

Our scaled-variable-reduced-coordinate (SVRC) framework for correlating saturation properties was used to represent the vapor pressures of a wide variety of refrigerants at temperatures from the triple point to the critical point. In general, the SVRC model represented the vapor pressures of refrigerants within their experimental uncertainties, when two adjustable parameters were used for each substance (average errors of 0.12%). More importantly, the SVRC framework shows excellent capability for generalized saturation property predictions. This is demonstrated by the predictions for vapor pressures, which yielded average errors of less than 1%, based on a single experimental vapor pressure measurement.

INTRODUCTION

Chlorofluorocarbons (CFCs) have been blamed for ozone layer depletion. Molina and Rowland (1) reported that photo-dissociation of CFCs in the stratosphere produces significant amounts of chlorine atoms, which catalyze the destruction of the ozone layer. As a result, the Montreal Protocol agreements of 1987 issued a ban on the production of CFCs after the year 2000. Hydrofluorocarbons (HFCs) represent a viable substitute to CFCs.

Design and operation of processes using alternative refrigerants requires accurate knowledge of thermophysical properties. Such properties are essential both when used directly in process development and equipment sizing, or when used as input to predictive models. Experimental data on vapor pressures of alternative refrigerants are limited. Although many accurate equations of state have been developed to address the property needs of specific refrigerants, they are limited in their range of applicability and/or lack of suitability for generalization.

In a previous study (2), a unified framework based on the corresponding states theory concepts was presented for the correlation of saturation properties. The main characteristics of the framework are: [1] ability to correlate the saturation properties with high precision over the full saturation range, [2] ability to satisfy established theoretical limiting behavior in the near-critical region, [3] suitability for generalization to provide predictive capability, [4] ability to predict the behavior of any refrigerant, and [5] simplicity. In the present study, we evaluate the abilities of this SVRC model in correlating the vapor pressures of refrigerants, as well as for predicting vapor pressures using generalized model parameters.

THE SVRC MODEL

Our general SVRC formulation for correlating thermophysical properties may be given as (2):

$$\left(Y_{\infty}^{\alpha} - Y^{\alpha}\right)/\left(Y_{\infty}^{\alpha} - Y_{0}^{\alpha}\right) = \Theta(\varepsilon) \tag{1}$$

or

$$Y^{\alpha} = Y_{0}^{\alpha}\Theta(\varepsilon) + \left[1 - \Theta(\varepsilon)\right]Y_{\infty}^{\alpha} \tag{2}$$

where

$$\varepsilon = (X_\infty - X)/(X_\infty - X_0) \tag{3}$$

and $\Theta(\varepsilon)$ = correlating function, X = correlating variable, Y = saturation property at given X, Y_∞ = asymptotic value of saturation property at X, Y_0 = initial value of saturation property at X_0 and α = scaling exponent.

For correlating saturation properties, Equation (1) is recast for representing the various properties between the triple and the critical points as:,

$$Y = \left\{ Y_c^\alpha - \left(Y_c^\alpha - Y_t^\alpha \right) \Theta \right\}^{(1/\alpha)} \tag{4}$$

where Y becomes p for vapor pressure, ρ for liquid density, etc. Applied specifically to vapor pressure correlation, the above equation is written as:

$$p = \left\{ p_c^\alpha - \left(p_c^\alpha - p_t^\alpha \right) \Theta \right\}^{(1/\alpha)} \tag{5}$$

where p_c and p_t are the critical and triple point pressures, respectively. The functions $\Theta(\varepsilon)$ and α are defined as (2)

$$\Theta(\varepsilon) = \frac{\left(1 - A^{\varepsilon^B}\right)}{(1 - A)} \tag{6}$$

$$\alpha = \alpha_c - \Delta\alpha \frac{\varepsilon(1 + C\varepsilon)}{1 + C} \tag{7}$$

where

$$\varepsilon = \frac{T_c - T}{T_c - T_t} \tag{8}$$

and

$$\Delta\alpha = \left(\alpha_c - \alpha_t \right) \tag{9}$$

and A, B and C are correlation constants, α_c and α_t are the values of α at the critical temperature and triple point temperatures, respectively.

Figure 1 illustrates the variation of the reduced vapor pressure with reduced temperature for a number of compounds with different degrees of acentricity and polarity. This figure shows the dependency of vapor pressure on temperature and chemical structure. In this framework (2), Equation (5) accounts

for the effects of temperature and chemical structure through the two functions (Θ and α), both of which are temperature dependent. Figure 2 presents the effect of reduced temperature on the correlating function, Θ, while Figure 3 depicts the variation of the scaling exponent, α, with reduced temperature, ε. Inspection of Figures 2 and 3 reveals that the correlation (3):

- provides a universal representation for scaled-and-reduced vapor pressures, Θ, in terms of the reduced temperature, ε, and
- accounts for variations due to the chemical structure through the limiting values of the scaling exponent (α_c and α_t).

Table 1 presents typical results of applying this framework to the correlation of vapor pressures and several other saturation properties (2, 3). While precise fits of experimental data were obtained using a two-parameter (α_c and α_t) model, fairly accurate *generalized* predictions were also realized. For example, in dealing with various chemical species, we have demonstrated previously (2) that reasonably accurate generalized vapor pressure predictions (average deviations of 1%) may be obtained using the following correlations for α_c and $\Delta\alpha$:

$$\alpha_c = C_1 T_{rt}^{C_2} + C_3 Z_c^{C_4} + C_3^{(Z_c - 0.29)} + C_5^{\omega} + C_6^{(3\omega - \omega/Z_c)} - 3.0 \qquad (10)$$

and

$$(\alpha_c - \alpha_t) = C_1 T_{rt}^{C_2} + C_3 Z_c^{C_4} + (C_1 - 1) T_{rt}^{C_4} + \left[C_3^{(Z_c - 0.29)} - 1.0\right] C_7 \qquad (11)$$

where T_{rt}, Z_c, ω and C_1 through C_7 are the reduced temperature at the triple point, the critical compressibility, the acentric factor and correlation parameters, respectively.

MODEL APPLICATION AND DISCUSSION

In this evaluation of the SVRC framework, 25 different pure-fluid refrigerants were used, twelve of them being alternative refrigerants, for a total of 2669 data points. Table 2 presents the sources and ranges of experimental vapor pressure data taken from the literature. Due to the lack of experimental measurements in the literature, most of the refrigerants studied here do not have data over the complete saturation range from the triple point to the critical point. Physical properties (specifically T_c, p_c, Z_c and ω) required to implement the SVRC model were obtained from the same literature source as the vapor pressure data, whenever possible.

The SVRC model contains five parameters (A, B, C, α_c and α_t), as shown by Equations (6-9). However, our studies have indicated that good precision is retained when A, B, and C are treated as universal constants applicable to all fluids. Table 3 presents the results obtained in this study for the refrigerants considered. Three case studies were considered, one to evaluate the model precision (Case 1) and two others (Cases 2 and 3) to address the quality of the predictions using a generalized-parameter model. For Case 1, we used a two-parameter model to regress α_c and α_t, and for Cases 2 and 3, we used the generalized correlations outlined earlier by Equations (10) and (11). Values for the correlation parameters are presented in Table 4.

The SVRC approach was used to correlate pure-fluid vapor pressures at temperatures between the triple point and critical point. However, the range of data for each fluid varied, due to the availability of data. When the triple point data were not available, the triple point terms were replaced by the lowest available temperature data point (T_i) for Cases 1 and 2 in Equations 5, 8 - 11. For convenience, we have also tested the quality of the predictions when the normal boiling point is used as the initial temperature value, as given by Case 3. The results from Case 1 demonstrate that the SVRC precisely represents vapor pressures of refrigerants with an average percent deviation (%AAD) of 0.12, which is typically within their experimental uncertainty. Our results also indicate that Case 3 produces better overall results than Case 2, as shown by the %AAD of 0.97 and 0.57, respectively. This may be due to the narrower temperature range used and to the larger uncertainty in the refrigerant data at lower pressures.

Although the SVRC model is essentially empirical, the results obtained here and previously (2, 3) offer good evidence of its usefulness in generalized predictions. This is demonstrated by the results for Cases 2 and 3, where generalized predictions yield average errors of less than 1.0% over the available range of data, based on a single experimental measurement. Figure 4 depicts the resultant deviations for the alternative refrigerants in Case 2.

SUMMARY

1. Our SVRC framework was used to correlate vapor pressures of a wide variety of refrigerants from the triple to the critical point.

2. The SVRC model can represent vapor pressures of refrigerants essentially within their experimental uncertainties (within 0.1%), when two adjustable parameters are used for each substance.

3. More importantly, the SVRC shows excellent generalized predictions of these vapor pressures, with average errors of less than 1%, based on available physical properties (T_c, p_c Z_c, T_b, ω).

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Table 1

Typical Results Using the Scaled-Variable-Reduced-Coordinate Framework

Physical Property	No. of Fluids	%AAD	
		Regressed Parameters	Generalized Parameters
Vapor Pressure	18/47	0.05	0.83
Liquid Density	22/34	0.10	0.82
Vapor Density	11/11	0.17	1.00
Interfacial Tension	13/23	0.33	1.00

Table 2

Sources of Vapor Pressure Data

Refrigerant	Temperature range (K)	Pressure range (bar)	No. of points	Source
R-11	218.34 - 291.23	0.0197 - 0.8282	32	4
R-11	236.49 - 293.06	0.0631 - 0.8855	7	5
R-11	353.15 - 378.15	5.2262 - 9.1267	7	6
R-12	213.19 - 293.15	0.2266 - 5.659	49	7
R-12	180.00 - 330.00	0.0225 - 14.1994	44	8
R-12	298.49 - 384.08	6.560 - 40.620	10	9
R-22	312.65 - 368.59	15.161 - 49.234	40	10
R-22	217.09 - 248.50	0.4665 - 2.0439	27	11
R-22	211.89 - 365.75	0.3512 - 46.53	13	12
R-22	180.00 - 340.00	0.0370 - 28.0670	46	8
R-22	299.73 - 364.24	10.928 - 45.421	9	13
R-23	141.06 - 298.19	0.0163 - 47.39	49	14
R-23	272.43 - 298.15	24.614 - 47.144	36	15
R-32	268.15 - 348.08	6.9056 - 54.091	19	16
R-32	191.20 - 351.56	0.1635 - 58.28	30	17
R-32	219.97 - 324.98	0.948 - 32.78	25	18
R-32	235.87 - 266.35	2.0035 - 6.5016	18	19
R-32	273.39 - 347.29	8.191 - 53.239	32	20
R-32	295.28 - 348.63	15.727 - 54.635	26	21
R-32	208.36 - 237.38	0.4943 - 2.1410	28	22
R-123	243.15 - 447.91	0.017 -31.720	47	23
R-123	388.14 - 453.14	3.300 - 34.563	45	24
R-123	271.55 - 308.06	0.2990 - 1.2990	15	25
R-123	273.15 - 457.38	0.344 - 37.453	39	26
R-123	256:40 - 453.79	0.1431 - 34.8770	104	27
R-123	300.65 - 373.17	1.0028 - 78.74	9	28
R-123	279.97 - 350.00	0.46 - 4.40	89	29
R-123	308.26 - 456.74	1.31 - 36.58	69	30
R-124	222.21 - 390.47	0.142 - 33.067	44	31
R-124	310.94 - 394.50	5.580 - 35.615	29	13
R-124	278.11 - 393.12	1.9557 - 34.7035	71	32
R-124	221.81 - 283.87	0.1361 - 2.3975	40	19

Table 2 (continued)

Sources of Vapor Pressure Data

Refrigerant	Temperature range (K)	Pressure range (bar)	No. of points	Source
R-125	290.00 - 339.00	11.069 - 36.065	12	33
R-125	275.56 - 323.87	7.237 - 25.843	10	34
R-125	275.65 - 335.16	7.2533 - 33.1383	30	35
R-125a	278.55 - 353.85	5.00 - 32.53	18	36
R-134a	214.44 - 313.20	0.1730 - 10.1771	60	11
R-134a	268.17 - 374.26	2.434 - 40.680	12	28
R-134a	253.15 - 373.15	1.332 - 39.672	26	26
R-134a	279.94 - 349.99	3.78 - 24.59	14	29
R-134a	279.15 - 363.15	3.6278 - 32.4089	43	37
R-134a	316.19 - 370.51	11.032 - 37.674	13	13
R-134a	210.96 - 369.14	0.1413 - 36.6386	33	38
R-134a	303.14 - 374.12	7.6985 - 40.5175	38	39
R-141b	253.82 - 356.01	0.1075 - 45.282	58	40
R-141b	270.92 - 312.31	0.2541 - 1.2911	31	25
R-142b	297.12 - 410.15	3.232 - 4.0383	70	41
R-142b	224.80 - 284.69	0.1487 - 2.1822	37	42
R-142b	319.99 - 400.01	6.32 - 33.88	13	43
R-143a	173.61 - 225.79	0.0349 - 1.0101	10	44
R-143a	280.00 - 339.98	7.69 - 33.37	13	18
R-143a	244.42 - 345.21	2.262 - 37.173	33	45
R-143a	295.00 - 342.00	11.635 - 34.737	12	46
R-152a	154.56 - 260.04	0.00065 - 1.6045	32	47
R-152a	273.15 - 386.00	2.636 - 44.815	45	48
R-152a	311.82 - 383.74	8.813 - 42.943	34	21
R-152a	219.92 - 273.14	0.2272 - 2.6373	39	42
R-152a	320.00 - 385.00	10.906 - 43.924	8	49
R-152a	301.44 - 386.12	6.5173 - 44.9201	56	39
R-152a	237.33 - 367.88	0.586 - 33.344	161	50
R-227ea	276.55 - 375.95	2.40 - 29.43	22	36
R-236ea	283.45 - 414.25	1.21 - 35.33	29	36
R-245cb	280.25 - 381.65	2.64 - 32.64	25	36
R-C318	232.19 - 388.36	0.1899 - 27.763	60	51

Table 3

Results for the Scaled-Variable-Reduced-Coordinate Framework as Applied to Refrigerants

Refrigerant	NPTS	*Case 1 (%AAD)	Case 2 (%AAD)	Case 3 (%AAD)
R-11	30	0.02	0.81	0.49
R-12	103	0.08	0.94	0.87
R-22	135	0.12	0.71	0.55
R-23	85	0.13	0.99	1.76
R-32	178	0.12	0.75	0.30
R-123	336	0.14	1.27	0.44
R-124	184	0.04	1.19	0.54
R-125	52	0.03	1.63	0.36
R-125a	18	0.15	0.89	2.17
R-134a	238	0.07	2.02	0.28
R-141b	89	0.04	1.10	0.35
R-142b	119	0.11	0.87	1.21
R-143a	68	0.06	0.69	0.60
R-152a	374	0.11	1.04	0.19
R-227ea	19	0.16	1.30	1.88
R-236ea	29	0.49	1.30	1.40
R-245cb	25	0.26	0.78	0.48
R-C318	60	1.24	1.19	1.54
C_1	114	0.02	0.34	
C_2	130	0.07	0.08	
C_3	54	0.07	0.36	
C_4	80	0.18	0.36	
Ar	58	0.03	0.34	
N_2	68	0.02	0.29	
NH_3	23	0.05	0.19	
Overall	2669	0.12	0.97	0.57

* Case 1. Two-parameter model used to regress α_c and $\Delta\alpha$ as system specific parameters.
Case 2. Generalized correlation from lowest temperature data to critical point, α_c and $\Delta\alpha$ from equations (10) and (11), respectively.
Case 3. Generalized correlation from normal boiling point to critical point, α_c and $\Delta\alpha$ from equations (10) and (11), respectively.

Table 4

Correlation Parameters as Reported by Shaver et al. (2)

Parameter	Value	Comment
A	2/3	Universal constants in all cases
B	0.985	
C	4/3	
C_1	0.433	Generalized constants for Cases 2 and 3
C_2	1.722	
C_3	0.775	
C_4	0.897	
C_5	0.799	
C_6	0.941	
C_7	2.643	

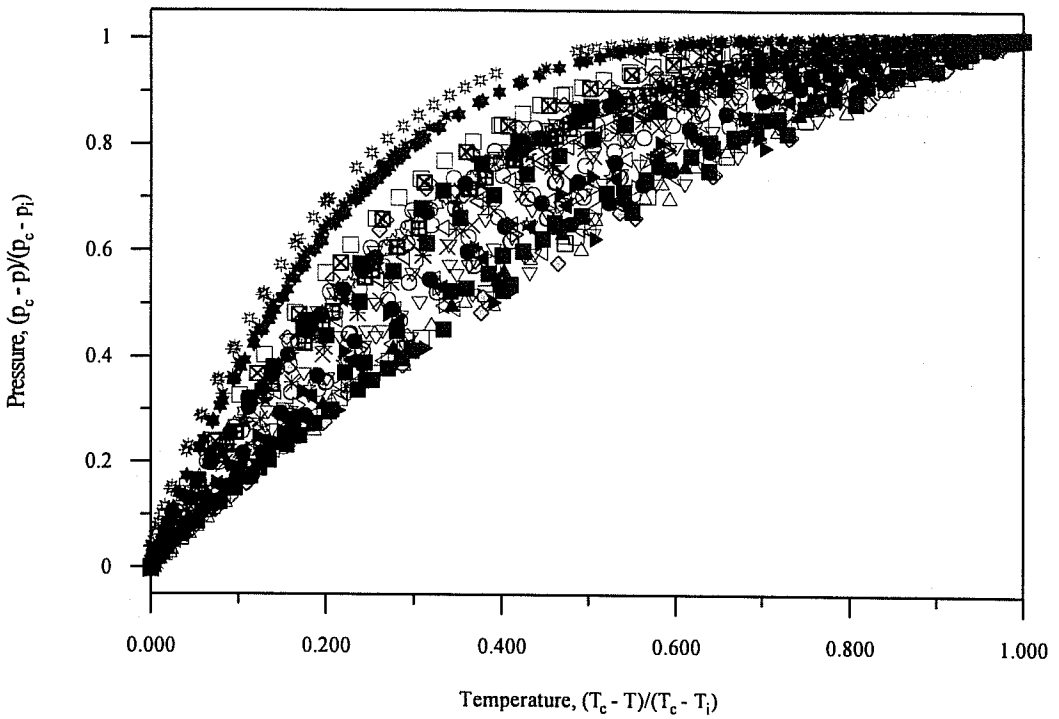
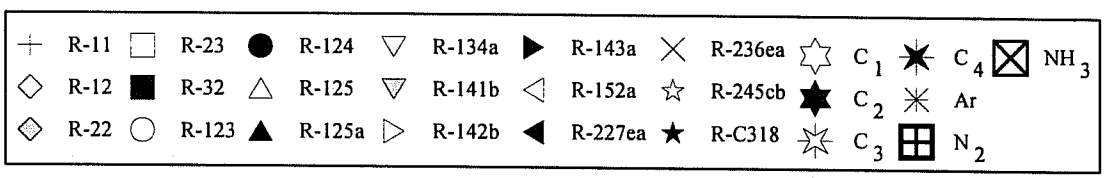


Figure 1. Vapor Pressure Variation with Temperature.



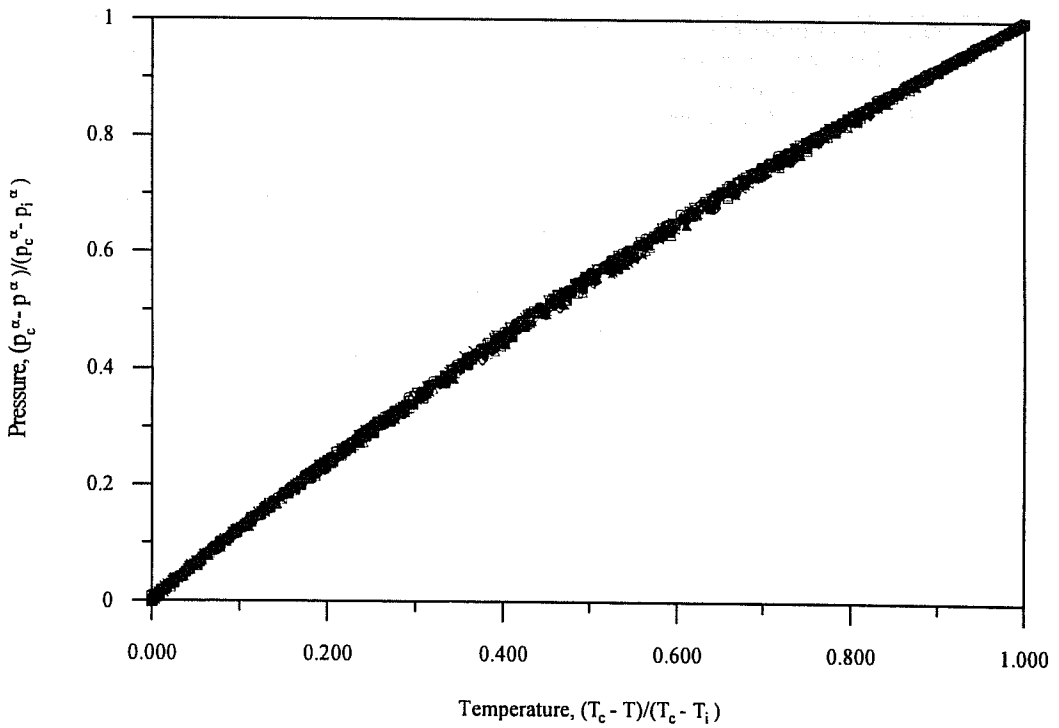


Figure 2. Effect of Temperature on the Correlating Function, Θ.

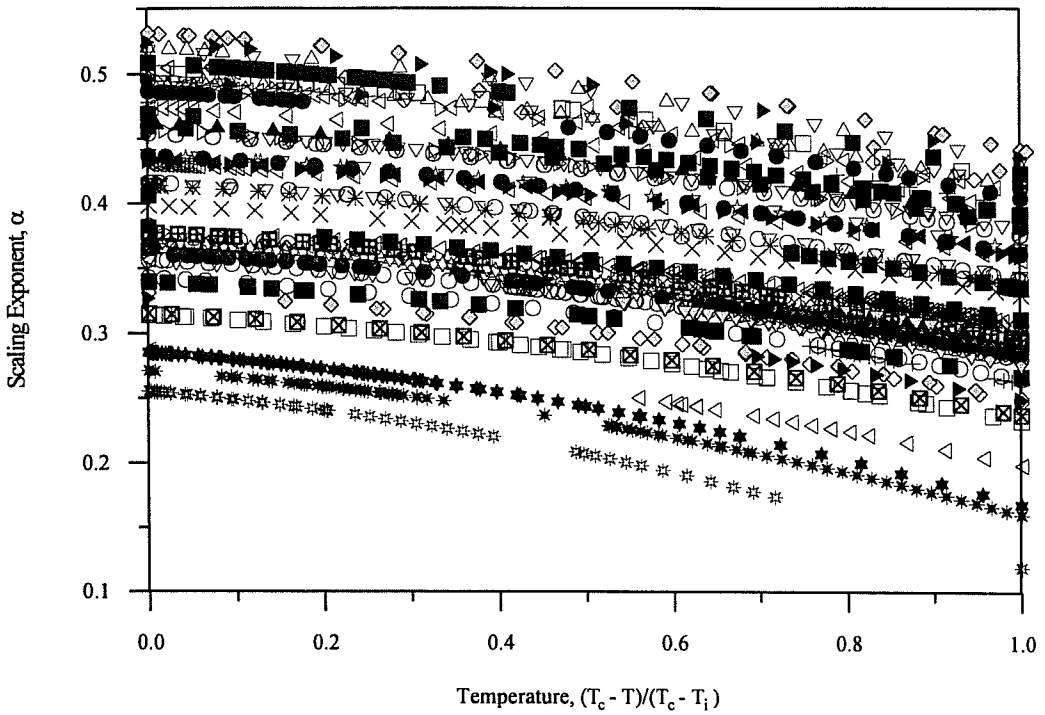


Figure 3. Effect of Temperature on the Scaling Exponent.

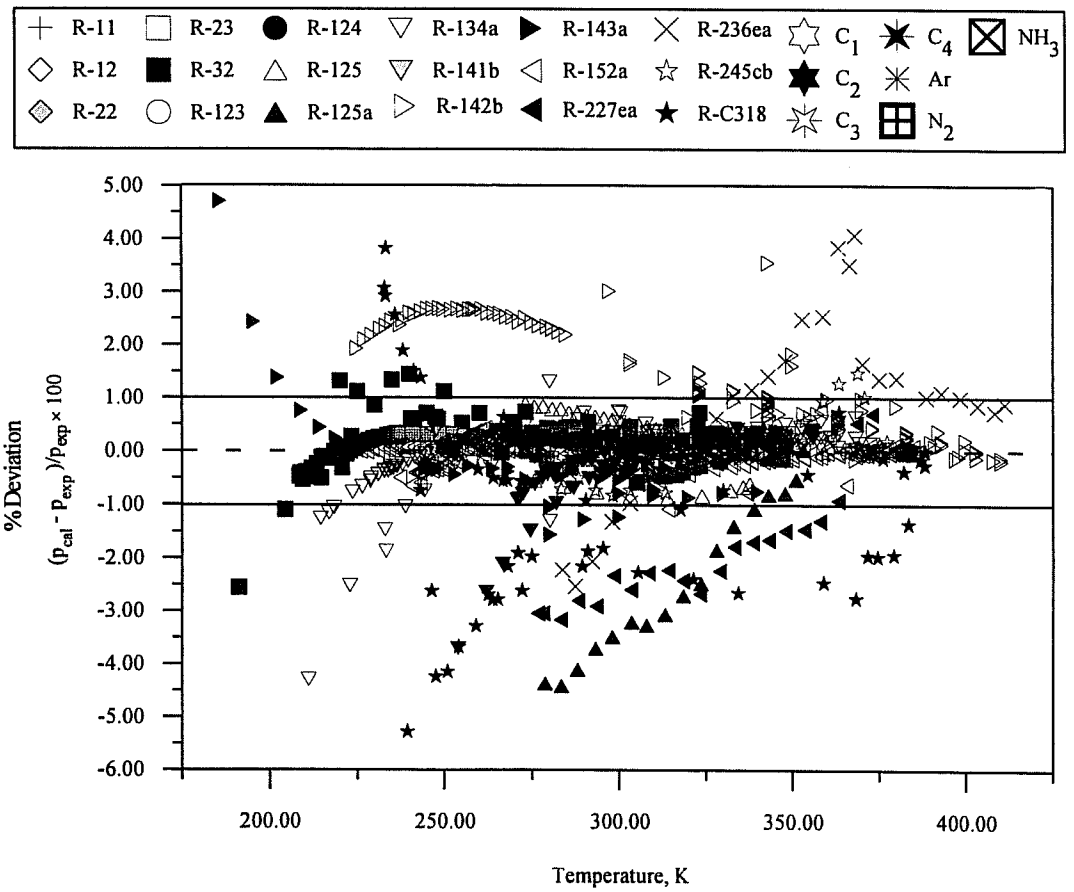


Figure 4. Deviations in Predicted Vapor Pressures for Alternative Refrigerants Using Generalized Parameters.

The Thermodynamic Performance of

Non-Azeotropic Refrigerant Mixtures

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Abstract:

A study of the thermodynamic performance of non-azeotropic refrigerant mixtures (NRAMS) involving R-143a/R-134a was completed. The aim of the study was to identify a possible replacement for R-12. Three refrigeration cycles were considered: the vapor-compression cycle, the internal heat-exchanger cycle, and the mixture-cascade cycle.

Our results suggest that while the overall thermodynamic performance of R-12 vapor-compression cycle is superior to the nonflammable compositions of R-143a/R-134a, the internal heat-exchanger cycle appears promising when these NRAM mixtures are used. Moreover, the mixture-cascade cycle yields poor performance using the NARM mixtures under study.

INTRODUCTION

Most of the current refrigerants, such as R-11, R-12 and R-502, are chemically inert chlorofluorocarbons (CFCs). Because of their inertness, they remain in the atmosphere for many years and ultimately diffuse into the stratosphere. Moreover, they have a low depletion rate since they have a low solubility in rain water and are very volatile. Molina and Rowland(1) discovered that the photo-dissociation of CFCs in the stratosphere produces significant amounts of chlorine atoms, which, in turn, catalyze the destruction of ozone layer. The ozone layer plays an important role in shielding the earth from ultraviolet radiation. Therefore, finding alternatives to CFCs is urgent. The Montreal Protocol agreements of 1987 were a consequence of this necessity. The deadlines for the phaseout of the CFCs have been established in this Protocol, and it has also been decided that no CFCs will be produced after the year 2000.

The main culprits in damaging the ozone layer are chlorine and the heavier halogens in refrigerants. Fluorine is the only halogen that is benign to the ozone layer. Hence compounds that do not contain such elements are sought as alternatives. The ozone depletion potential (ODP) is a parameter that indicates the relative amount of chlorine or heavier halogens in a refrigerant. By this definition, any compound that does not contain the culprit halogens has an ODP of zero.

Non-azeotropic refrigerant mixtures (NARMs) behave differently from pure fluids or azeotropic or near-azeotropic mixtures. They are a combination of two or more refrigerants that do not form an azeotrope at any composition and offer other special characteristics. At saturation, they exhibit different compositions in the liquid and the vapor phases. Unlike the pure refrigerants or azeotropic mixtures, the phase transformation of NARMs does not occur at a constant temperature. The temperature rises during evaporation and falls during condensation and this change in temperature is called the temperature glide. This behavior of NARMs can be exploited for energy savings in various refrigeration cycles. In a counter-current heat-exchanger, the composition of a NARM may be adjusted so that the gliding temperature during phase change matches the temperature profile of the source or sink fluid. When this match is achieved, the irreversibilities of heat exchange are minimized and the COP is improved. The temperature change in the condenser allows a considerable change in the heat sink temperature, which substantially reduces the sink flow rate for a given heat load. The temperature glide is directly proportional to the difference in the normal boiling points of the constituents in the NARMs.

The thermodynamic performance of CFC refrigerants is excellent; therefore, the task of finding their alternative is not an easy one. Some hydrochlorofluorocarbon (HCFC) compounds like R-22 have been considered as temporary replacements for the CFCs because of their shorter atmospheric lives. However, HCFCs do contain chlorine and they too will be phased-out. The

hydrofluorocarbon (HFC) compounds considered as replacements for R-12 are R-152a and R-134a. ASHRAE Standard(3) suggests that R-152a is non-toxic, but flammable. Calm(4) argues that the current price of R-134a is much higher than other refrigerants. He predicts that the price will continue to fall, but R-134a will not be cheaper than R-12 until after 1995. The properties of a large number of other compounds considered as alternatives are not as good as those of the CFCs, and no single compound possesses all the qualities required of a good refrigerant. They do possess some qualities but all lack many of the desirable features of R-12. Hence, mixtures of compounds of different qualities have been proposed to serve as refrigerants. These mixtures are expected to possess the desirable properties of individual components and eliminate the undesirable features. In particular, mixing a nonflammable refrigerant with a flammable one can help in suppressing the flammability.

Downing(5) asserts that halogenated compounds are very good at producing nonflammable mixtures at relatively low concentrations. For example, the flammable range for propane in air is about 2.2 to 9.5 vol. %. If nitrogen is used to eliminate the flammability of propane, an additional 43% of nitrogen should be added to the mixture. However, the same job can be achieved using about 10 to 13% R-12. Richard and Shankland(6) experimentally determined the nonflammable compositions of several refrigerant mixtures. Data for such mixtures are presented in Table 1. However, the thermodynamic performances of the mixtures were not evaluated.

The thermodynamic performance of a refrigerant is judged by such parameters as the coefficient of performance (COP), the volumetric capacity, the compressor outlet temperature and pressure, and the lowest achievable temperature in the evaporator. Other desirable properties of a refrigerant are low flammability and low toxicity. The COP is obtained by dividing the net refrigerating effect by the energy of compression. The volumetric capacity is expressed as the ratio of the net refrigerating effect to the refrigerant volume flow rate at the compressor inlet.

The motivation for this study is to seek a replacement for R-12 that could match or approximate the performance of R-12. The normal boiling point of R-12 is -21.7 °F and therefore it is the lowest temperature achievable by R-12 without causing leaks in the evaporator. Hence R-12 can be used to cool a source fluid to 0 °F in the evaporator. Food products such as meat, vegetables and fruits can be preserved by refrigeration at 0 °F. We endeavored to study the non-flammable compositions of the NARM R-143a/R-134a for this purpose. According to Koelet(2), both R-143a and R-134a have zero ODP and both possess good thermodynamic characteristics. Furthermore, the flammability of R-143a is suppressed by the presence of R-134a.

CYCLE PERFORMANCE EVALUATION

The thermodynamic performance was computed in the vapor-compression as well as in two other refrigeration cycles, namely, the internal heat-exchange cycle and the mixture-cascade cycle. The schematic diagram for each of these cycles is presented in Figure 1. The vapor-compression cycle is the simplest of the three cycles. However, the most widely used method for achieving the benefits of NARMs is the internal heat-exchange cycle, where the throttling losses are reduced. The main idea in the internal heat-exchange cycle is that the liquid leaving the condenser is sub-cooled by heat-exchange with the vapor leaving the evaporator. The mixture cascade cycle is specially useful for achieving low evaporator temperatures. Here, only a part of the vapor condenses. The resulting liquid richer in the less volatile component is used to condense the vapor in a condenser/evaporator. Hence, the liquid leaving this unit is rich in the more volatile component. The throttling and subsequent evaporation of this liquid give the lowest temperature in the cycle.

The refrigeration process in these cycles was simulated using the ASPEN-PLUS simulator. To validate the simulation results, two test simulations were performed on R-12 in a vapor-compression cycle, and the results were compared to those of Bivens et al.(7) In this comparison, the Soave-Redlich-Kwong (SRK) equation of state (EOS) was employed to evaluate the cycle performance at the same conditions as reported by Bivens and coworkers. The simulations were performed to fulfill a duty of one ton by cooling an arbitrary source fluid from 10 to 0 °F. Air available at 100 °F was used as a heat sink. The pressure drop in the heat-exchange units was ignored for simulation purposes. The compression process was simulated by the ASPEN-PLUS model "Compr" while the separator in the Mixture Cascade cycle was simulated by the model "Flash2"; all other units were simulated by the model "Heater". The comparison is presented in Table 2, which indicates that Biven and coworkers have used a 100% efficiency for the compressor. We have also included simulation results for 72% compressor efficiency because the efficiencies of most of the compressors lie in the range of 65 to 80%.

Having established the reliability of the process simulations, we proceeded to evaluate the thermodynamic performance of the three cycles using two specific cases:

Case 1: A 10 °F approach at the evaporator inlet and the condenser outlet. This means that the working fluid should enter the evaporator at -10 °F. Also, the liquid from the condenser should exit at 110 °F since air is available as the heat sink at 100 °F.

Case 2: A 20 °F approach at the evaporator inlet and the condenser outlet. This means a temperature of -20 °F at the evaporator inlet and 120 °F at the condenser outlet.

A counter-current flow pattern was assumed in the evaporator and the condenser, and a 72% compressor efficiency was employed. Five different mixtures were considered in our evaluations. As indicated by Table 3, these mixtures contain from 10 to 46% R-143a mole fraction.

RESULTS AND DISCUSSION

The vapor-compression and the internal heat-exchange cycles were evaluated using the conditions outlined by Cases 1 and 2 described above. However, the mixture-cascade cycle was evaluated only for Case 2 because it has been reported to work well only with high temperature lifts and with low temperatures in the evaporator.

1. The Vapor-Compression Cycle

A comparison of the coefficient of performance (COP) of R-12 and R-143a/R-134a mixture in this cycle is presented in Figure 2, which also shows a comparison with the COP of R-12 in the vapor-compression cycle. The temperatures and pressures at the inlet and outlet of the compressor are presented in Tables 3 and 4.

The results show that the R-143a/R-134a mixtures considered in this study require higher pressures at compressor outlet than R-12. In general, the pressure of the system increases as the amount of R-143a in the mixture increases. For Case 2, the mixture composition 10% R-143a/90% R-134a requires a sub-atmospheric pressure in the evaporator. Therefore, this composition should not be employed in Case 2, otherwise leakage of surrounding air into the evaporator will destroy the integrity of the system. The post-compression temperatures of the mixtures are lower than that of R-12. This means that increasing the pressure of these mixtures will pose fewer problems to the seals and other critical components in the system. As expected, the COP values are higher for Case 1, where the average temperatures in the evaporator and the condenser are closer. The COP of R-12 is higher than that of the mixtures studied, for both Cases 1 and 2.

Another important performance parameter is the volumetric capacity which is depicted in Figure 3. The volumetric capacity indicates the volume of the refrigerant that must be circulated in order to fulfill a given refrigeration duty. The results show that, in general, the volumetric capacity increases as the percentage of R-143a in the mixture increases. This means that mixtures richer in R-143a require lower flow rates in the refrigeration circuit. However, if the main interest is to get a performance closer to that of R-12, 10% R-143a/90% R-134a is the choice for Case 1 and 20% R-143a/80% R-134a is the choice for Case 2.

The compression ratio, the temperature glide in the evaporator and the throttling loss (vapor fraction after expansion) are presented in Table 5. These

results show that the mixtures under investigation require a higher compression ratio than R-12. The compression ratio decreases as the percentage of R-143a in the mixtures increases. As the composition of the mixture is changed from 10% R-143a to 46% R-143a, the temperature glide increases gradually. The temperature glides of the mixtures considered indicate that the magnitudes are much smaller than expected by the difference in the boiling points of the constituents. One reason for this may be the large throttling losses as reported in Table 5. Also, the larger throttling losses of these mixtures compared to those of R-12 are responsible for the lower COP of the mixtures.

2. The Internal Heat-Exchange Cycle

The magnitudes of the COP of the refrigerants under investigation are presented in Figure 4. The observed trend is similar to that produced by the vapor-compression cycle, and this is also true for the volumetric capacity as shown in Figure 5.

The percentage increase, in the COP and the volumetric capacity using the internal heat-exchange (IHX) cycle is presented in Tables 6 and 7. The results show that the NARMs mixtures yield more improvement than R-12. Hence, evidently the use of this refrigeration cycle is more beneficial for the NARMs than for pure refrigerants.

Table 6 and 7 indicate that for mixtures, the percentage improvement in both the COP and the volumetric capacity increases with the increase in R-143a content up to 40% R-143a. For the 46% R-143a/54% R-134a mixture, the improvement is less than that for 40% R-143a/60% R-134a.

The temperature and pressure of the compressor inlet and outlet for this cycle are presented in Tables 8 and 9. The compressor outlet pressure is identical to that observed for vapor-compression cycle. For R-12, the inlet pressure and temperature also remain the same, but they are increased slightly in all other cases. However, there is a significant increase in the temperature of the vapor leaving the compressor, albeit, the values are still within safe limits. Again, for Case 2, the composition 10% R-143a/90% R-134a is not suitable because it requires a sub-atmospheric pressure in the evaporator. The compression ratio, the temperature glide and the throttling loss are presented in Table 10. Some improvement in the temperature glide and some reduction in the compression ratio are realized in this cycle, compared to the vapor-compression cycle. However, the reduction in throttling loss is significant as calculated in Table 11.

3. The Mixture-Cascade Cycle

The mixture-cascade (MC) cycle was simulated only with the conditions prescribed by Case 2, as discussed previously. The COP and the volumetric capacity decrease significantly in this cycle, as shown in Figures 6 and 7.

Nevertheless, a similar trend is observed; the maximum COP is yielded by mixtures with less R-143a, and the maximum volumetric capacity (in the range of nonflammable composition) is given by the 46% R-143a/90% R-134a mixture. The percentage drop in the COP and the volumetric capacity, relative to these parameters in the vapor-compression cycle (Case 2 results), is presented in Table 12. The possible reasons for this deterioration in performance may be the increased throttling losses observed in mixture cascade cycle as presented in Table 13. The only positive result of this cycle is the lower compression ratio, for all the compositions studied, as shown in Table 14. However, the overall performance clearly shows that the mixture under investigation is not suitable for use in this cycle.

CONCLUSIONS

1. Our results suggest that the internal heat-exchange cycle is more useful for the NARMs than for pure refrigerants. This is well demonstrated by the performance results using R-143a/R-134a mixture. Energy savings are expected by adopting the internal heat-exchange cycle, and higher COP and volumetric capacity can be reached by using this cycle with a lower compression ratio.

2. The mixture-cascade cycle is not useful for the NARMs investigated. The COP and the volumetric capacity deteriorate in this cycle. However, this cycle requires the minimum compression ratio among the cycles studied.

3. The overall thermodynamic performance of R-12 vapor-compression cycle is superior to that of the nonflammable compositions of the R-143a/R-134a mixture in the cases studied.

4. In general, for the cycles considered, increasing the R-143a content decreases the COP but increases the volumetric capacity of the resulting mixture. In addition, mixtures lean in R-143a show better thermodynamic performance than mixtures richer in R-143a. We have also observed that closer approach temperatures between the refrigerant and the heat source and between the refrigerant and the heat sink give better COP and volumetric capacity and requires lesser compression ratio. However, closer approach temperatures in the heat-exchangers require increased area for heat transfer.

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Table 1

Mixture Flammability at Room Temperature

Mixture	Flammable Component/Diluent	Critical Flammability Ratio (mol%)	Difference in Normal Boiling Points of Components (°C)
A	HFC-32/HFC-125	81.6/18.4	7.2
B	HFC-143a/HFC-134a	46.6/53.4	20.9
C	HFC-152a/HFC125	38.5/61.5	19.5
D	Propane/HFC-125	17.4/82.6	2.3
E	HFC-152a/HCFC-22	49.6/50.4	15.8
F	HFC-152a/HCFC-124	45.5/54.5	14.8
G	HFC-152a/HFC-134a	20.3/79.7	1.7

Reference: Richard and Shankland (1992)

Table 2

Theoretical Cycle Comparison

	Bivens et al. (1989)	This study ($E_{comp.}$ = 1)	This study ($E_{comp.}$ = 0.72)
COP	3.35	3.38	2.58
Compressor Discharge Temp (°C)	84.4	84.4	99.4
Suction Pressure (kPa)	355.8	357.8	357.8

Conditions:

4.4 °C	Evaporator Temperature	15.6 °C	Compressor Suction Temperature
65.6 °C	Condensing Temperature	54.4 °C	Expansion Device Temperature
1723 kPa	Compressor Outlet Pressure		

Table 3

Compressor Inlet and Outlet Pressure for Vapor-compression Cycle

% R-143a	Compressor Outlet Pressure (kPa)		Compressor Inlet Pressure (kPa)	
	Case 1	Case 2	Case 1	Case 2
10	1227.3	1406.5	126.7	97.9
20	1310.0	1496.2	138.9	107.4
30	1392.7	1606.5	152.2	117.7
40	1475.5	1709.9	166.7	129.1
46	1523.7	1765.1	176.0	136.5
R-12	1061.8	1206.8	132.2	105.0

Table 4

Compressor Inlet and Outlet Temperature for Vapor-compression Cycle.

% R-143a	Compressor Outlet Pressure (°C)		Compressor Inlet Temperature (°C)	
	Case 1	Case 2	Case 1	Case 2
10	72.3	82.6	-22.7	-28.3
20	73.1	83.3	-22.1	-27.8
30	73.6	84.3	-21.7	-27.4
40	73.8	84.8	-21.3	-27.1
46	73.8	84.8	-21.2	-27.0
R-12 for comparison	78.2	89.8	-23.3	-28.9

Table 5

Compression Ratio, Temperature glide and Throttling Loss for Vapor-Compression Cycle.

% R-143a	Compression Ratio		Temperature Glide (°C)		Throttling Loss	
	Case 1	Case 2	Case 1	Case 2	Case 1	Case2
10	9.7	14.4	0.65	0.56	.4457	.5121
20	9.4	13.9	1.22	1.06	.4558	.5227
30	9.1	13.7	1.68	1.46	.4655	.5374
40	8.9	13.2	2.03	1.77	.4749	.5502
46	8.7	12.9	2.17	1.91	.4804	.5563
R-12 for comparison	8.0	11.5	0.00	0.00	.3937	.4527

Table 6

Improvements in COP by the Use of Internal Heat-exchange Cycle.

% R-143a	Case 1 COP			Case 2 COP		
	IHX Cycle	VC Cycle	% Increase	IHX Cycle	VC Cycle	% Increase
10	1.903	1.811	5.08	1.483	1.378	7.62
20	1.889	1.785	5.82	1.465	1.354	8.20
30	1.868	1.759	6.19	1.440	1.311	9.84
40	1.850	1.738	6.47	1.408	1.278	10.17
46	1.830	1.726	6.04	1.392	1.265	10.04
R-12 for comparison	1.967	1.915	2.73	1.564	1.490	4.71

Table 7

Improvements in Volumetric Capacity by the Use of Internal Heat-exchange Cycle.

% R-143a	Case 1 Volumetric Capacity (kJ/m^3)			Case 2 Volumetric Capacity (kJ/m^3)		
	IHX Cycle	VC Cycle	% Increase	IHX Cycle	VC Cycle	% Increase
10	825.9	777.5	6.22	595.2	546.2	8.96
20	888.0	828.5	7.19	638.3	580.5	9.96
30	949.2	881.2	7.71	682.7	610.0	11.93
40	1014.3	935.5	8.42	724.6	642.4	12.79
46	1046.4	968.3	8.06	748.6	664.7	12.63
R-12 for comparison	824.5	801.8	2.83	621.9	592.2	5.03

Table 8

Compressor Inlet and Outlet Pressure for Internal Heat-Exchange Cycle.

% R-143a	Compressor Outlet Pressure (kPa)		Compressor Inlet Pressure (kPa)	
	Case 1	Case 2	Case 1	Case 2
10	1227	1407	128	99
20	1310	1496	141	109
30	1393	1606	155	120
40	1475	1710	170	132
46	1524	1765	179	140
R-12 for comparison	1062	1207	132	105

Table 9

Compressor Inlet and Outlet Temperature for Internal Heat-Exchange Cycle.

% R-143a	Compressor Outlet Temperature (°C)		Compressor Inlet Temperature (°C)	
	Case 1	Case 2	Case 1	Case 2
10	103.3	120.2	-22.5	-28.1
20	103.2	119.9	-21.8	-27.5
30	102.8	119.9	-21.2	-26.9
40	102.2	119.6	-20.8	-26.6
46	102.1	119.4	-20.7	-26.4
R-12 for comparison	110.8	130.0	-23.3	-28.9

Table 10

Compression Ratio, Temperature glide and Throttling Loss for Internal Heat-exchange Cycle.

% R-143a	Compression Ration		Temperature Glide (°F)		Throttling Loss	
	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2
10	9.6	14.2	0.84	0.76	0.3408	0.3923
20	9.3	13.7	1.54	1.42	0.3509	0.4043
30	9.0	13.4	2.10	1.95	0.3621	0.4156
40	8.7	12.9	2.49	2.32	0.3704	0.4291
46	8.5	12.6	2.63	2.47	0.3784	0.4374
R-12 for comparison	8.0	11.5	0.00	0.00	0.2966	0.3372

Table 11

Percentage Drop in Throttling Loss by using Internal Heat- Exchange Cycle.

% R-143a	Case 1			Case 2		
	IHX Cycle	VC Cycle	% Increase	IHX Cycle	VC Cycle	% Increase
10	0.3408	0.4457	23.54	0.3923	0.5121	23.39
20	0.3509	0.4558	23.01	0.4043	0.5227	22.65
30	0.3621	0.4655	22.21	0.4156	0.5374	22.66
40	0.3704	0.4749	22.00	0.4291	0.5502	22.01
46	0.3784	0.4804	21.23	0.4374	0.5563	21.37
R-12 for comparison	0.2966	0.3937	24.66	0.3372	0.4527	25.51

Table 12

Drop in COP and Volumetric Capacity by the Use of Mixture Cascade Cycle.

% R-143a	COP			Volumetric Capacity (kJ/m^3)		
	MC Cycle	VC Cycle	% Drop	MC Cycle	VC Cycle	% Drop
10	0.600	1.378	56.4	245	546	55.2
20	0.581	1.354	57.1	252	581	56.6
30	0.576	1.311	56.1	274	610	55.1
40	0.567	1.278	55.6	287	642	55.3
50	0.569	1.265	55.0	304	665	54.3

Table 13

Temperature Glide and the Percentage Increase in Throttling Loss by using Mixture Cascade Cycle.

% R-143a	Temperature Glide (°C)		Throttling Loss		
	MC Cycle	VC Cycle (Case 2)	MC Cycle	VC Cycle (Case 2)	% Reduction
10	--	--	--	--	--
20	1.08	1.06	0.5172	0.5227	1.05
30	1.84	1.46	0.5268	0.5374	1.97
40	1.73	1.77	0.5352	0.5502	2.73
46	2.22	1.91	0.5381	0.5563	3.27

Table 14

Comparison of the Compression Ratios for the Vapor-compression, the Internal Heat-exchange and the Mixture Cascade Cycle.

% R-143a	Compression Ratio		
	Vapor Compression (Case 2)	Internal Heat Exchange (Case 2)	Mixture Cascade
10	--	--	--
20	13.9	13.7	13.4
30	13.7	13.4	12.7
40	13.2	12.9	12.3
46	12.9	12.6	11.8

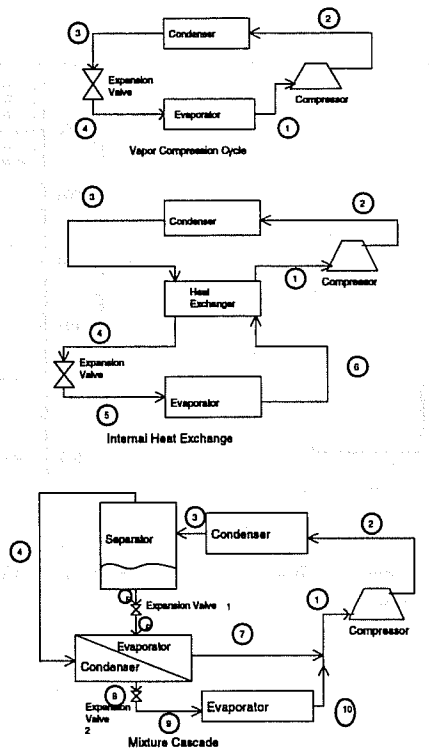

Figure 1. The Refrigeration Cycles Which Can Be Used for Exploiting the Benefits of NARMs

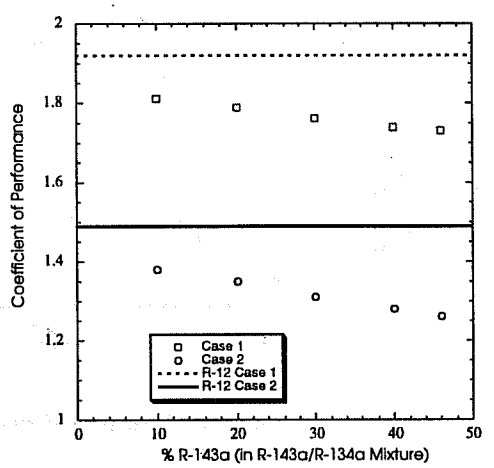

Figure 2. Coefficient of Performance in the Vapor-Compression Cycle

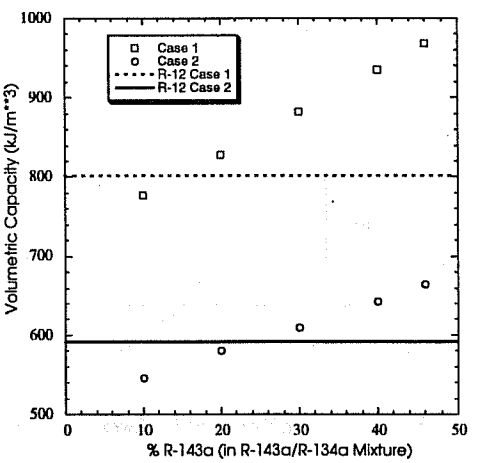

Figure 3. Volumetric Capacity in the Vapor-Compression Cycle

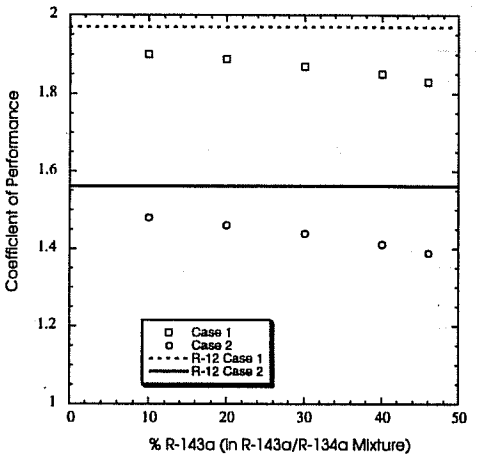

Figure 4. Coefficient of Performance in Internal Heat-exchange Cycle

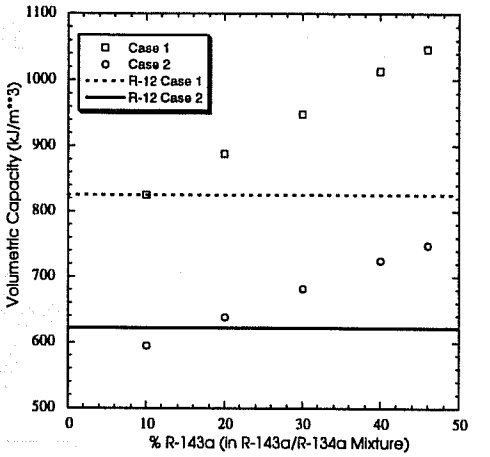

Figure 5. Volumetric Capacity in Internal Heat-exchange Cycle

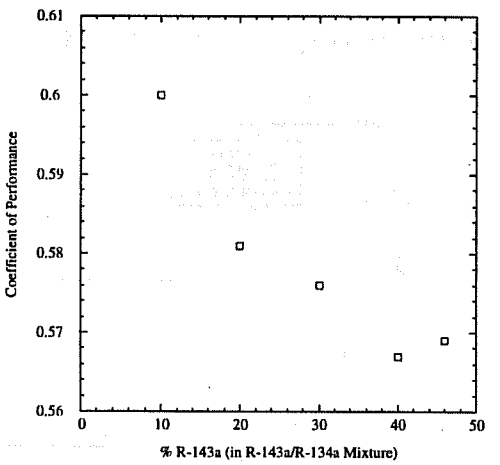

Figure 6. Coefficient of Performance in Mixture Cascade Cycle

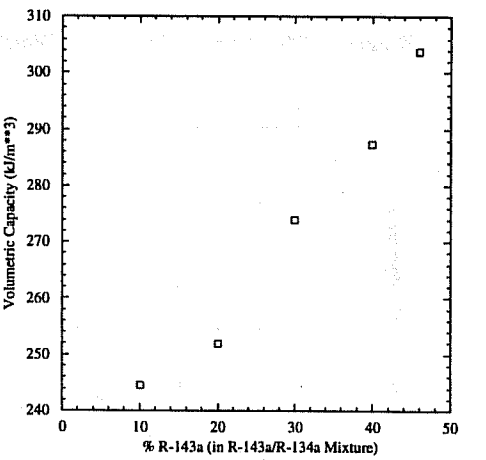

Figure 7. Volumetric Capacity in Mixture Cascade Cycle

Pollution Prevention Activities in an Arctic Oil Field

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Abstract:

The Kuparuk River Field on the Alaskan Arctic North Slope has an aggressive pollution prevention program. Due to its remote location, facilities include a camp to support up to 1,000 workers in addition to three production facilities, 42 remote drillsites, a crude oil topping unit and a small airport. Field support activities such as fleet vehicle and heavy equipment maintenance, corrosion inspection and prevention, and processing equipment maintenance are performed on-site. Most years, significant construction activities occur. Kuparuk also serves as a base for nearby oil exploration activities.

The pollution prevention program is the foundation of the field's waste management strategy. Founded in 1989 as a grassroots effort focused primarily on office wastes, the program has expanded into maintenance and production areas and is now fully integrated into daily work processes.

Prevention activities include reduced chemical use, equipment and process modifications as well as aggressive fluids recycling in either the hydrocarbon process stream or the enhanced oil recovery system. Examples of projects from exploration, production and field support will be provided.

Introduction:

The Kuparuk River Oil Field, operated by ARCO Alaska, is the second largest oil field in North America. The field is located adjacent to the Beaufort Sea in northern Alaska. The nearest village, which has only 200 residents, is 40 miles to the west. All community services such as housing, medical care, snow removal, power generation and transportation must be provided to support industrial activities including exploration, production, processing and transportation of oil.

The development area covers more than 400 square miles of land leased from the State of Alaska. The discovery well was drilled in 1969 and production began in 1981. Kuparuk has three central oil production facilities and 42 active drillsites. It is estimated that the recoverable reserves are 2 billion barrels (Bbl). Oil is pumped 45 miles from Kuparuk to Pump Station 1 of the Trans-Alaska Pipeline (TAPS).

Due to Kuparuk's remote location, waste management becomes an expensive cost of doing business. The nearest landfill, approximately 50 miles to the east, charges $1,300 per 27 cubic yard dumpster. This landfill is rapidly filling up with no alternative site planned. Alaska has no hazardous waste disposal facilities; therefore, all hazardous waste must be transported greater than 2,000 miles for handling. Onsite waste management activities are complicated by freezing conditions and expensive labor and equipment.

Therefore, the focus of the Kuparuk Waste Management Strategy is pollution prevention. If no waste is generated, nothing needs to be collected, transported or managed. This strategy is based on the desire to protect public health and the environment; reduce operating costs; and reduce risk for criminal liability, civil liability, and cleanup costs. It depends on employee motivation, and has helped establish a positive company image in the community.

The cornerstone of the Kuparuk waste management strategy is a strong training program. The strategy depends on having educated personnel in the field routinely make complex waste management decisions. Just as the federal laws governing waste management place the burden of identifying a hazardous waste on the waste generator, the Kuparuk program places a large burden of responsibility on generators. For this reason, pollution prevention training is the key to success in a low cost environment.

Pollution prevention is the foundation of the Kuparuk waste management program (Fig. 1). Waste minimization activities build on this foundation by reducing, but not eliminating, cost and risk. Through reuse and recycling programs, valuable resources are placed back into service as usable materials. The following types of pollution prevention activities are used to achieve pollution prevention: volume reduction; good housekeeping; spill prevention; inventory control; process modification; reuse and recycle; chemical substitution; and technology changes and research development.

Historical Background:

Kuparuk's first waste minimization activities were initiated in the late 1980s as a grass-roots effort. A group playfully named the Group for Environmental Enhancement at Kuparuk, or GEEK, focused efforts on recycling paper, newspaper, and aluminum cans. This was a volunteer group, so a philosophy of participation based on individual responsibility developed.

Recycling locations were centralized and individuals were expected to accumulate materials, periodically bringing them to the central locations. Centralized locations were chosen to encourage substituting recycling for disposal. For example, newspapers are collected in the camp lobby, where housekeeping staff bundle them for recycling rather than disposal.

Other GEEK programs focused on reduced use such as replacing individual serving canned juices with juice dispensers and providing alternatives to single serving condiments. Many employees pack lunches to eat at facilities, so Styrofoam® use is widespread. GEEK initiated a program to offer reusable dishes in the self-prepared lunch rooms in addition to the dining hall.

In conjunction with these activities, an environmental awareness training session was developed. The training stressed "reduce, reuse, recycle" . A brief summary of this information was included in new employee orientation training. At the same time, chlorinated solvent use was severely restricted.

GEEK had local support, but it had no company imprimatur. By 1990 national regulatory attention was focused on minimizing hazardous waste, and a corporate waste minimization tracking and reporting program was developed. Each individual operating company was allowed the flexibility to develop its own program. Kuparuk chose to build on the existing GEEK model.

A central committee representing all departments was established to set goals. Boundary conditions established then still guide the program: projects must be economically viable, and only data that help manage pollution prevention are tracked. Some data is tracked, but the focus is on evaluating and implementing. Most waste minimization models are developed as stand-alone programs; the Kuparuk program is based on an inclusion principle: integrate projects into daily work processes and subject them to the same project planning criteria (efficiency, cost-benefit, and value) on which other projects are judged. All pollution prevention ideas are eligible for consideration in several recognition programs.

Although the initial committee meetings were painfully absorbed with identifying program sideboards and committee structure, gradually the focus shifted to brainstorming projects. Each department successfully set goals and was able to show measurable success at the end of the year. In the process, each group developed its own approach to managing wastes generated in its activities.

This is an overview of a very successful pollution prevention program that evolved from concept into reality. Grass-roots efforts developed into a formal program with full support of employees and management. Costs and volumes are only "snap-shots" due to dependence on work activity levels. Projects are divided into subjects for the reader's ease; many projects are successful only through the efforts of inter-departmental teams. It is impossible to credit all who made these ideas reality.

Camp Housing and Office Activities:

Since many Camp Services staff were GEEK members, this Department continued to target lifestyle changes. Some of the first projects focused on living quarters. Water conservation was encouraged by installing low-flow shower heads; variable-level washing machines replaced single-level machines. Wall-mounted liquid soap dispensers replaced individual bars of soap. The practice of providing a stack of Styrofoam® cups next to the sinks in sleeping quarters for individual single use was discontinued, and a multi-use plastic glass was provided instead.

Office activities began to adapt electronic communication into daily routine to reduce paper use. The local phone directory is distributed via electronic mail instead of paper copies. Training required under the Process Safety Management regulations uses interactive electronic "books." Common information sources are found on electronic file servers. Kuparuk has also begun expanding its information distribution network on company web sites.

Laser-printer toner cartridges are reconditioned up to 17 times before the components are recycled. This core recycling program has saved an estimated $13,000 per year since 1992 and reduced an average of 43 pounds of solid waste for every cartridge that is purchased (2.5 pounds saved for each reconditioning).

Refrigerant recycling was identified as a viable project; purchase of approximately 300 pounds of refrigerant per year was avoided. Several years later Federal regulations were implemented which required refrigerant recycling.

Camp Services paired with the Materials group to develop cardboard recycling programs and an information materials exchange for office supplies. Existing recycling programs for paper and aluminum were expanded to include materials generated at facilities and satellite wash locations such as rig camps and construction sites.

Materials Management:

The Materials Department was the first department to appreciate fully the concept of life-cycle costs and used this concept to identify waste minimization projects. Transportation and warehousing costs are significant components of using materials in the Arctic. Kuparuk has 58,000 square feet of heated storage and 200,000 square feet of yard space to store an inventory valued at $38 million, not including the value of construction materials used for capital projects. Non-capital parts and material consumption is $9.5 million annually.

In 1990 nearly all chemicals were ordered as drum stock. Now the only materials ordered in drums are those few products whose useage does not warrant ordering in bulk. Everything else is ordered in railroad cars and other reuseable containers. Reducing drum stock not only reduces purchasing, transportation and warehousing costs, it also reduces disposal costs. Historically, empty drums were stored until summer then burned to remove all residual chemicals. This time-consuming process was eliminated and replaced with a washing operation. Wash waters are now recycled in enhanced oil recovery operations and the washed drums are recycled.

Sometimes it is the simple solution that is the most elegant. Kuparuk spends approximately $8 million annually to transport freight; a larege amount of scrap banding material is generated in the process. These narrow metal strips are impossible to recycle because they are difficult to package and handle cost-effectively. Impossible to recycle unless you own a scrap banding machine, a grinder attached to the top of a 55 gallon drum, that chops the band into five-inch pieces. Then scrap metals dealers are pleased to accept the high-quality metal. The pilot scrap banding recycling effort saves an estimated $5,000 annually and is not labor or maintenance intensive.

Prior to 1991, Kuparuk was buying pallets to stage materials at specific job sites. At the same time, pallets used for shipping materials to Kuparuk were discarded at the unloading point. At a cost savings of $45 per pallet plus disposal costs, it was obvious that implementing a reuse program made sense. The existing inventory tracking system was utilized to track the location and "stocking" levels of numerous reusable materials.

Fleet Maintenance:

The fleet is comprised of more than 360 light vehicles, 165 pieces of heavy equipment and 370 pieces of non-mobile support equipment. Vehicle maintenance staff systematically reviewed each waste stream and developed programs to eliminate or recycle these wastes. Fleet maintenance activities are similar nationwide and there are many proven waste reduction techniques. While adapting "proven" techniques, the Kuparuk vehicle maintenance staff has moved well beyond those horizons.

Lube oil and antifreeze is recycled. A hot-water parts washer eliminated the need for a solvent washer. Lead-acid batteries were put on a core recycling program through a distributor. Expensive disposable rags were replaced with a rag washing service provided by a dry cleaner, eliminating 8,000 pounds of waste annually. Oil, air and fuel filters comprised a large portion of the waste stream.

An advertisement about reusable filters in a racing magazine caught someone's attention. The idea was discussed at the morning meeting. A manufacturer was called. Soon the vehicle and heavy equipment fleet was fully retrofitted with reusable oil filters, some were designed to meet Kuparuk's specifications.

The oil filter program was more successful than originally anticipated. The reusable filter has a washable screen to trap impurities. When the screen is washed the metal particles are inspected; these help pinpoint needs for worn parts. Results are more timely than those obtained in the traditional lube oil monitoring program; in only a few months an estimated $45,000 was saved by quick response to needed repairs. Kuparuk eliminated their $6,000 per year lube oil monitoring program (1).

The oil filter program's sucess inspired a similar evaluation for air filters. A washable filter was found that saved approximately $4,100 annually. The payback on light vehicles is less than a year; for heavy vehicles it is almost 3 years.

Think of the tires for all those vehicles! In the past, tires were run to destruction and sent to the landfill. Retreading had been evaluated over the years, but retreaded tires were deemed inferior products. A re-evaluation of this option showed that technological improvements had been made in retread quality. A core recycling program was established. Tires are monitored for tread-depth during routine preventive maintenance checks and returned to a tire distributor for retreading. Retread tires are returned to service at Kuparuk.

Spill Prevention:

The spill prevention ideas presented are only a small sampling of the hundreds of ideas implemented every year. Other examples are interspersed throughout this paper. Vehicle and road maintenance staff also targeted spill prevention as a pollution prevention activity. Each fall, gravel drillsites are sprayed with water until several inches of ice are built up. This protective layer prevents small spills from contacting and contaminating the gravel surface. In the event of a spill, the contaminated ice is chipped up, melted, and the fluids recycled.

Hose failures are one of the most common causes in oil field spills. Lubricators on well-work equipment were prone to periodically spraying a mist of hydraulic oil. Vinyl "splints" wrapped around the lubricator tip and fastened with Velcro® straps were developed to prevent this release. A sorbent pad inside the vinyl catches drips.

Construction:

As with many industries, oil field construction mobilizes and demobilizes frequently with a core company staff and many contractors mobilizing and demobilizing. Construction staff initially had a difficult time identifying ways to reduce waste. A group that initially thought there was not much it could do -- its first target was to reuse survey lath -- soon found that the best approach was to look at overall pollution prevention.

The change in drillsite pad construction methods is a good example of integrated pollution prevention. The initial impetus for reducing pad size from 65 acres to less than 11 acres was to reduce wetlands impact. When viewed from a broader perspective the reduced pad size also means smaller gravel pits with less overburden generated. Fewer trips to haul the gravel means less road maintenance, less diesel fuel usage, less waste associated with equipment maintenance and less cost on capital projects. Cost is something construction people understand!

New generation drillsite modules are also smaller. Smaller modules mean less materials and less cost. New technologies were required to allow shrinking the pads and modules. Wells were initially set on 120-foot spacing. New rigs and directional drilling advances now allow wells to be as close as 12.5 feet apart. Faced with the rising costs of North Slope wellhouses, the Drill Site Development team set out three years ago to reduce the $28,000 per wellhouse price tag. Each year Kuparuk needs about 40 new wellhouses as additional wells are drilled.

Teamwork and innovation resulted in a new generation of wellhouse kits that cost about $14,000 each. The structure is assembled on site for $3,500.

In the winter, temporary ice roads and pads are another technique used to reduce road gravel needs. Constructed of snow or ice approximately 6 inches to 8 feet thick, ice road and pad surfaces are removed whenever there is evidence of a spill; the ice is melted and reused as drilling make-up water or recycled in the enhanced oil recovery process. Snow roads costs approximately $16,000/mile and ice roads approximately $21,000/mile. This compares to $800,000/mile for a gravel road five feet deep with a 32 foot crown.

Soon cardboard, scrap wood and used pallet recycling collection points were established at construction job locations. Surplus programs were no longer just a way to eliminate waste but became useful recycle and reuse programs. In 1996 seven miles of 10-inch pipeline was relocated instead of installing new pipe.

Production Support:

The pipeline monitoring program uses radiography and coupons to measure corrosion rates. Metal coupons placed in pipelines monitor conditions and measure corrosion rates. After coupons are removed, they must be cleaned so corrosion damage can be evaluated. Prior to 1992 a chemical cleaning process was used which generated waste acids and solvents. This process was replaced with a mechanical system which eliminated personnel exposure to hazardous chemicals and reduced the volume of hazardous waste produced. Annual cost savings were approximately $11,000 the first year and $16,000 in subsequent years.

The radiographic inspection program generates a silver-contaminated fixer solution. Prior to 1994 an on-site two-stage electrolytic-ion exchange process was used to recover the silver, so the fixer fluid could be recycled. A periodic opportunity assessment showed that new technologies were available and the system was replaced with a single-stage ion-exchange process. The fixer is pumped through a series of ion-exchange cylinders in a closed-loop system. The depleted cylinders are returned in a core recycling program to the manufacturer who recovers the silver. The new process reduces spill potential, analytical costs, record keeping, and the volume of contaminated rags generated.

The on-site production laboratory uses a variety of solvents for testing crude and chemicals and for cleaning glassware and instruments. Used solvents are collected and redistilled for reuse. Initially a mixed solvent distillate was tested for cleaning glassware. Source separation has become feasible; and now solvents are reused for analytical purposes. The purchase of toluene was reduced from 105 gallons to ten gallons the first year the program was implemented.

Approximately 3,000 pounds of inoperable small stainless steel valves were discarded annually until Maintenance staff found a creative way to implement a valve repair program, saving an estimated $265,000 per year. In this case, the primary obstacle to recycling was participation, not technical roadblocks. Participation increased when program "champions" made large, colorful signs explaining the economic benefits of recycling the valves. Collection containers staged at key locations encouraged participation.

Snow melt and rainwater that accumulate in Kuparuk's 128 reserve pits must be removed each summer. Clean snow is removed from the pits in spring to reduce the volume of water handled--2 million Bbl each year. Remaining fluid was hauled to a central location and injected into a disposal well. Eight 400-Bbl tanker trucks were used round-the-clock for eight weeks to transport fluids.

A pilot program to inject fluids into produced water enhanced oil recovery wells was initiated after the fresh pit water was tested for its compatibility with reservoir sands. At selected drillsites, water was pumped from the pit directly to wells. An unexpected side benefit of the program was discovered. Kuparuk reservoir rock breaks down when water is injected at higher than normal pressures. Preliminary results of the dewatering pilot suggest that high pressure breakdown is enhanced by injecting the cold (32 degree F) pit water. Not only was oil production enhanced, but eight high pressure breakdown jobs were deferred - a costs savings of $280,000. The program has been expanded to additional Kuparuk drillsites and other North Slope oil fields.

Facilities, Drill Sites and Well Maintenance:

Cross-tundra water injection lines are part of the enhanced oil recovery waterflood system. These lines require frequent internal cleaning (pigging) to remove solids and reduce corrosion. Historically, lines were pigged to lined surface pits; subsequently the fluids were removed and transported by vacuum trucks to a disposal well. A full-field pilot test was initiated to study if it was possible to stop diverting fluids to surface pits by allowing pigging effluent to be injected into the enhanced oil recovery injection wells; in other words, keep the fluids in the pipe and return the solids to the reservoir. A total of 580 miles of produced water and 370 miles of seawater lines were pigged in 316 separate events. The pilot test confirmed that reservoir plugging would not occur; a full-field program was implemented in 1993. In addition to approximately $290,000 annual savings for reduced labor and vacuum truck costs, spill potential was reduced and exposure of wildlife to oily water in open pits was eliminated.

A small problem remained; fluids trapped in the pig launchers/receivers still had to be released to open pits. The process was changed and a closed-loop blowdown system to redirect fluids back to the production stream. Eliminating all surface discharge to the pits reduced the need to clean pit liners and the safety hazards associated with working on the slippery liner surface.

Downhole pressure is often measured with a Panex® pressure gauge run on wireline. Power is supplied to the Panex® by industrial-grade alkaline batteries enclosed within the tool body. These batteries are in use from several hours to several days. New batteries are used for each run due to the high cost of a failed run relative to the cost of new batteries. When the downhole work is complete, the batteries are still quite usable. Since they are industrial-grade and are used for such a short time, they frequently have as much or more life left than a standard grade battery. In the past these batteries were discarded. A reuse program has since been set-up; these used batteries are now restocked in the central warehouse.

Drillsite test separators are sandjetted with diesel to remove sand and sediments. Standard operating practices have been to drain sandjet fluids into open top tanks, decant the fluids into vacuum trucks for transport to a hydrocarbon recycle facility and transport the solids to an oily-solids storage facility for batch recycling. This process is not only labor and equipment intensive; spill potential is also significant. A new procedure has been developed to return sandjet fluids to the process system via the production flowlines. Use of this procedure is limited by facility design.

Drilling and Exploration:

Exploration in the Arctic breeds mavericks. Small groups of hard-working people toil on a remote frontier of frozen arctic tundra or in crowded conditions on offshore rigs. These drillers pride themselves on their efficiency and innovation. That is the approach Kuparuk Drilling staff applied to waste minimization. When they decided to participate in the cardboard recycling program, they adapted a mud box to hold stored cardboard, minimizing the amount of handling required.

To reduce the use of heavy metals, they switched to a non-leaded pipe dope. Pipe is shipped from the factory with the non-leaded dope, rather than a factory-specified dope, so solvents are no longer used to clean the threads. Thread protectors are returned to the vendor where they are washed, inspected and reused.

Drilling finally made scrap wood recycling possible. Collecting the wood was easy; finding someone to use it was more difficult. Drilling staff worked with the State of Alaska Corrections System to develop a program where wood is donated to a correctional facility to fuel their wood-burning heating system. Scrap wood recycling has become so successful that the program was recently expanded to also donate used wood to a used construction materials outlet store. The program is now administered by the Materials group; when projects savings were last estimated in 1994, $60,000 in disposal costs were saved annually.

In the past, drilling operations produced large volumes of lubricating muds and rock cuttings which were discharged to surface pits. The first pollution prevention change for this waste stream was product substitution to reduce toxicity. Whenever possible, oil-based muds are replaced with more benign water-based mud systems. Mud systems have been modified to filter out rock cuttings and reuse the mud in a closed-loop recycling system. Cuttings are routed through a ball mill where they are ground up and pumped down the annulus of the previously drilled well. This closed-loop process reduces the amount of mud used for each job and also eliminates surface discharge. Since exploration is a winter activity in the Arctic, temporary storage areas are constructed of ice which is chipped up, melted and reinjected with the rock cuttings at the end of the job.

Brine is used in workover and completion jobs - more than 51,000 Bbl was used in 1992. Only slightly more than 22,000 bbl was purchased due to a brine recovery unit. Before 1988 brines were used only once; now they are reclaimed and reused an average of 2.25 times (2). Waste brine volumes have been reduced 25-75% per well depending on the type of workover operation and the type of brine used. The average savings for 1988-94 were more than $1.8 million dollars - PER YEAR! That figure does not include cost reductions for labor or not transporting and

disposing of more than 130,000 Bbl of used brine. Nor does it include the savings realized from recycling recovered crude.

Summary

Kuparuk's pollution prevention program began as a grassroots effort. Key to its continued success is its inclusion into core business processes. The program is clearly supported, but not entirely driven, by management. Individual departments work within their project team "personalities" to integrate pollution prevention into work processes. It is this inclusion principle that generates the synergy to sustain work process improvement.

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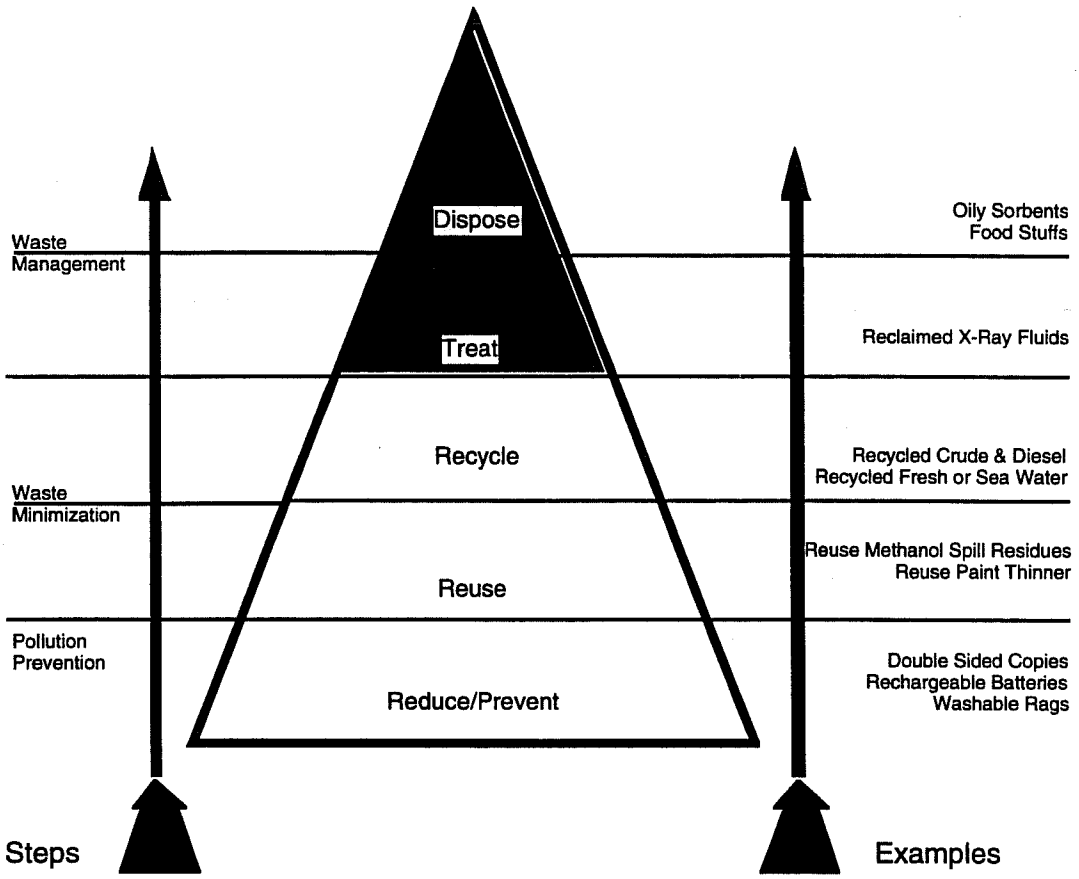
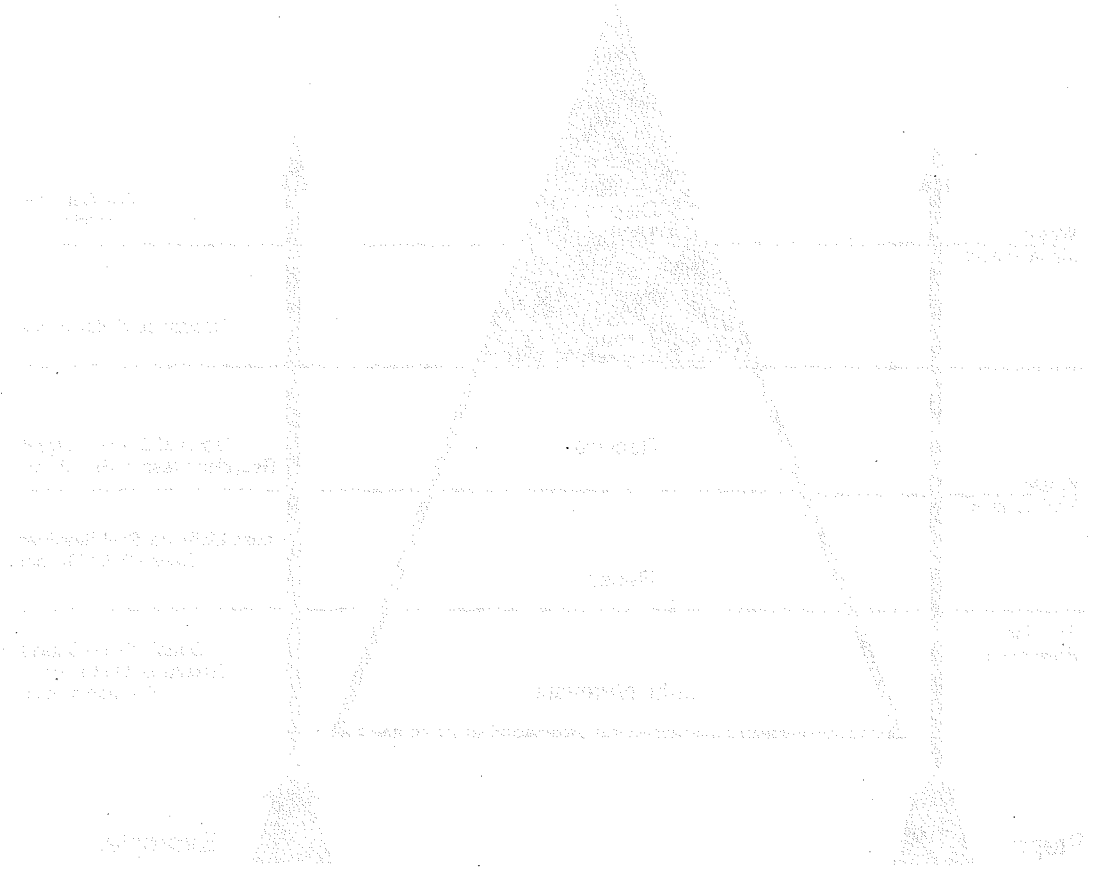


Figure 1: Pollution Prevention Triangle



Treatment and Remediation of Petroleum Hydrocarbons

BIOREMEDIATION OF OIL CONTAMINATED SOILS

A RECIPE FOR SUCCESS

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ABSTRACT

Bioremediation of land crude oil and lube oil spills is an effective and economical option. Other options include road spreading (where permitted), thermal desorption and off-site disposal. The challenge for environmental and operations managers is to select the best approach for each remediation site.

Costs and liability for off-site disposal are ever increasing. Kerr-McGee's extensive field research in eastern and western Texas provides the data to support bioremediation as a legitimate and valid option. Both practical and economical, bioremediation also offers a lower risk (of Superfund clean-up exposure) than off-site disposal.

Goals of the research were to:

1. Verify that bioremediation is a satisfactory option for remediating crude oil and lube oil contaminated soils in E&P operations.

2. Determine the critical factors that control the bioremediation process.

3. Develop a bioremediation program "recipe" for E&S and Operations to meet a variety of field conditions.

All three goals were met. This paper includes both results and conclusions of the study.

OIL SPILLS

In the exploration and production of oil and gas the accidental release of oil can occur at various stages. The industry installs safety and environmental controls, and develops operational procedures to prevent spills. However despite their best efforts once a spill occurs the company(s) works diligently to clean the environment. The type of oil may be crude oil or refined product. In the past the spilled product was "remediated" by one of the following methods: road spreading (where permitted), thermal desorption, or off-site disposal. The options of road spreading and off-site disposal created further potential liability and therefore did not always appeal. Thermal desorption was not always acceptable due to the lack of thermal desorption companies in the immediate area, the concern for air emissions, and the extremely high operational cost.

BIOREMEDIATION STUDY

In the last five to seven years the successful use of bioremediation (aerobic or anaerobic) on various organic remediation projects led Kerr-McGee Corporation to investigate this option. Bioremediation, the degradation of organic substances by microorganisms, has been studied by scientists since the early 1950's (Riser-Roberts 1992).[1] However the widespread use of bioremediation on crude oil or lube oil spills had not been proven in field situations. Therefore, Kerr-McGee's U.S. Onshore Region began a field test to determine the effectiveness of aerobic bioremediation for crude oil and lube oil contaminated soils. Two active oil and gas sites in Texas were chosen for the study. The two sites had different environmental conditions (East Texas had a higher annual precipitation rate than West Texas). This allowed the study to compare the various environmental factors to the effectiveness of bioremediation. A random-block statistical design was used on both sites.

STUDY RESULTS

The East Texas site, involved a lube oil-contaminated soil. The study began in the fall of 1990 and was completed in the fall of 1993. Two compressor sites were chosen for the lube oil study. The controllable factors were: soil nutrients, organic material, oxygen, and oil & grease content. The following amendment rates were used: fertilizer rates (5 lbs./100 sq. ft. and 12 lbs./100 sq. ft.) and organic rates (25 lbs./100 sq. ft. and 50 lbs./100 sq. ft.). The treatment areas

were tilled on two different schedules (two times/month or four times/month). This variation in tillage allowed Kerr-McGee to determine tillage effect (the addition of oxygen to the soil/microbes) on the degradation rate.
Results of the three year study indicated that the optimum fertilizer rate and organic material rate for bioremediation of a lube oil soil was 12 pounds/100 sq. ft. and 25 pounds/100 sq. ft., respectively (at the .05 alpha level). It was also noted visually that the weekly tillage rate was more effective on the degradation rate. Additional tillage increased the oxygen content and produced additional microbes and/or provided a more acceptable environment.

The second study site was a former emergency blowdown pit located in West Texas. The pit was contaminated with crude oil and produced water. The study began in the winter of 1991 and was completed in the fall of 1993. The controllable factors at this site were: soil amendments, nutrients, water or moisture content of the soil, oxygen, and oil & grease content. Two fertilizer rates (4 lbs./100 sq. ft. and 10 lbs./100 sq. ft.) and three organic material rates (25 lbs./100 sq. ft., 50 lbs./100 sq. ft. and 75 lbs./100 sq. ft.) were used. Fresh water was available for irrigation, enabling the correlation of soil moisture with degradation rate.

Results indicated that the optimum fertilizer rate and the optimum organic material rates for bioremediation of the crude oil soil were respectively, 14 lbs./100 sq. ft and 75 lbs./100 sq. ft. (significant at the .05 alpha level). The irrigated plots exhibited a faster rate of degradation than the dry-land plots. The irrigated plots with a soil moisture content of 14% or greater provided the microorganisms with a more suitable environment (Deuel 1994).[2]

CONCLUSION

In conclusion, the study results showed bioremediation to be a good alternative for the remediation of petroleum contaminated soils. From the study, generic amendment rate(s) were developed. The tillage rates should be no less than once per week to insure an adequate amount of oxygen to the microorganisms. The soil moisture content should be monitored to insure the water content is at least 14 percent. Further studies will be conducted in 1995 - 1997 to determine the effectiveness of bioremediation in colder climates such as in the Rocky Mountain states.

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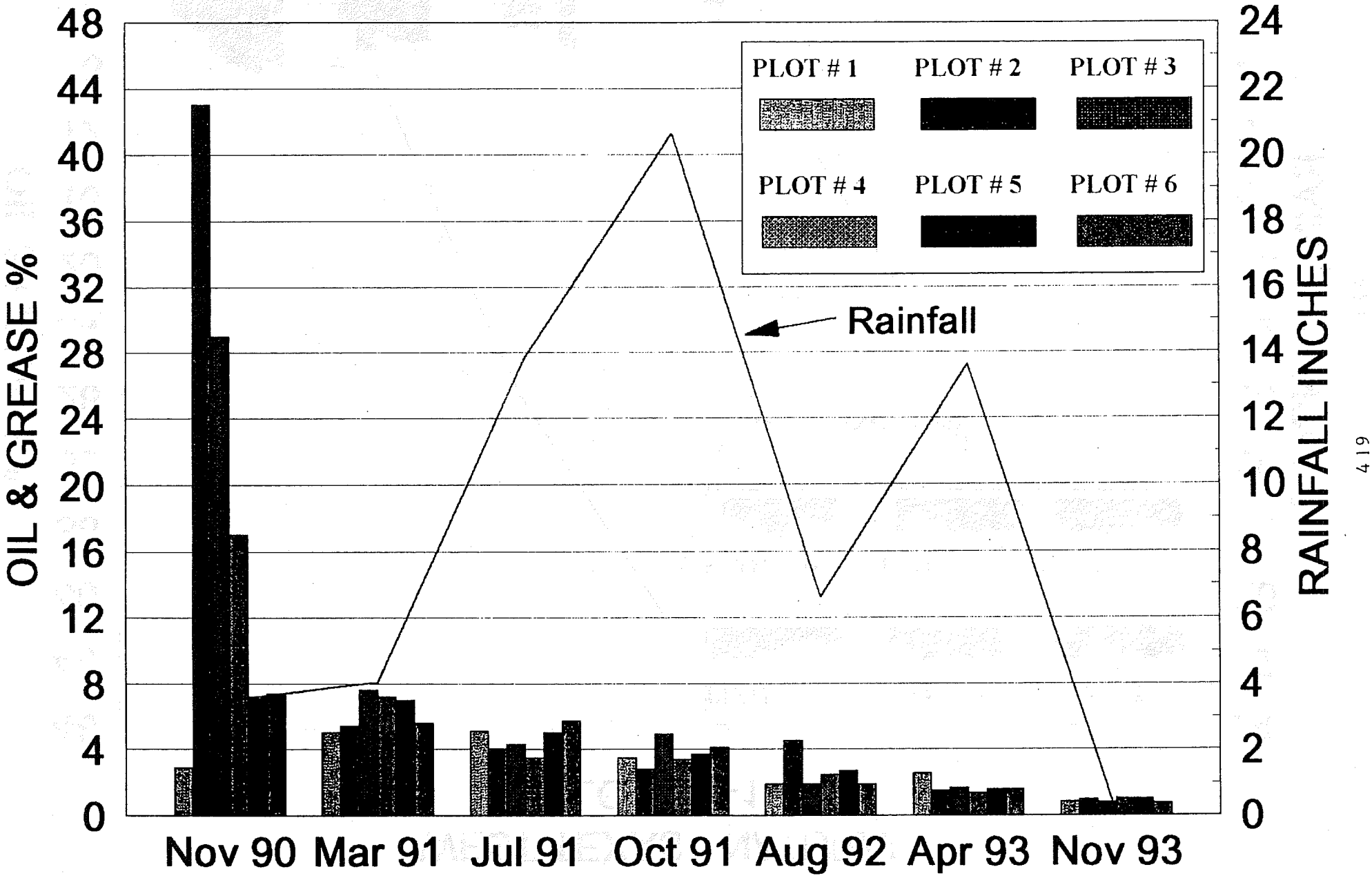
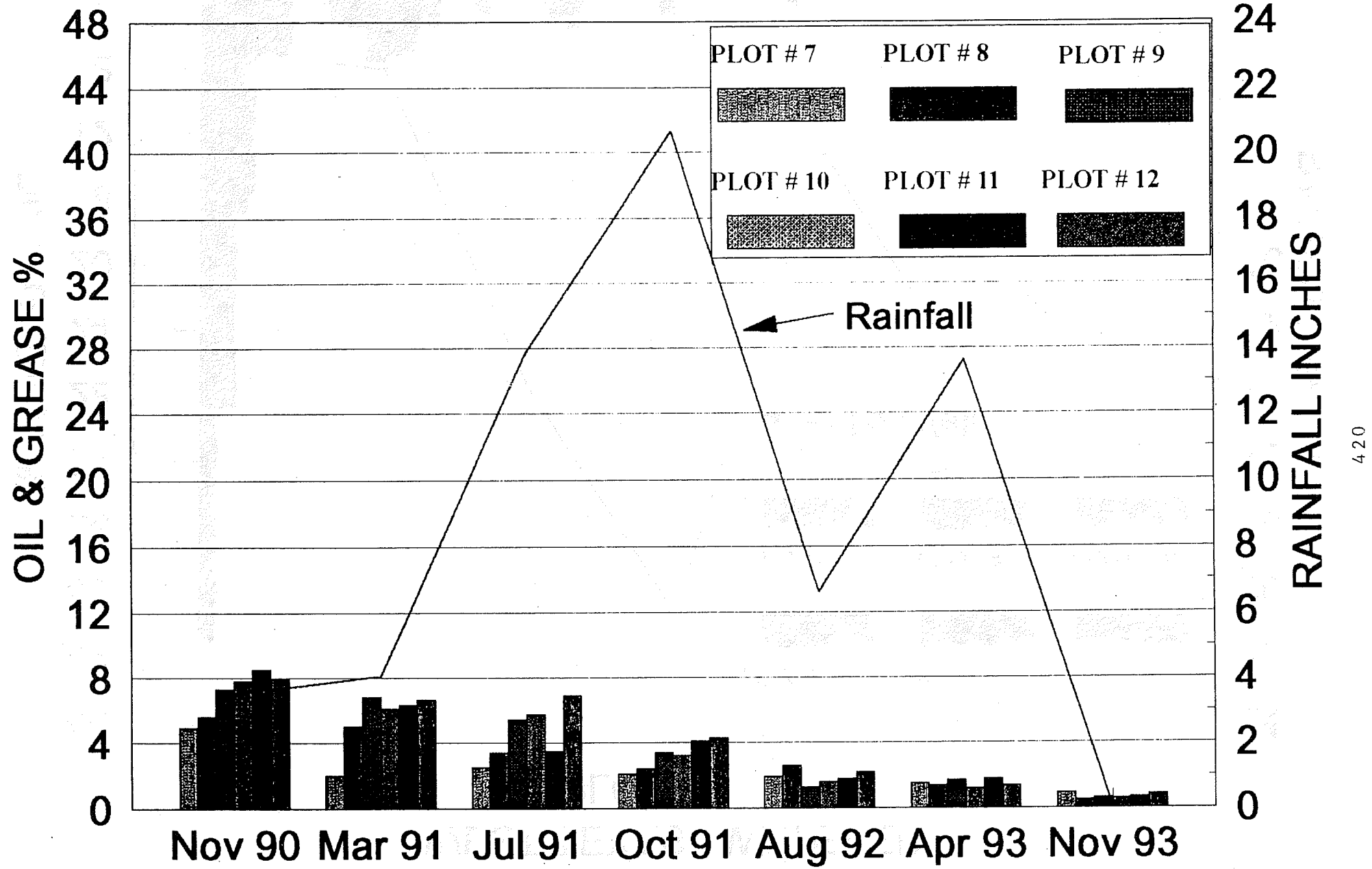
WEST TEXAS - WATERED
PLOTS 1 - 6



WEST TEXAS - NATURAL
PLOTS 7 -12



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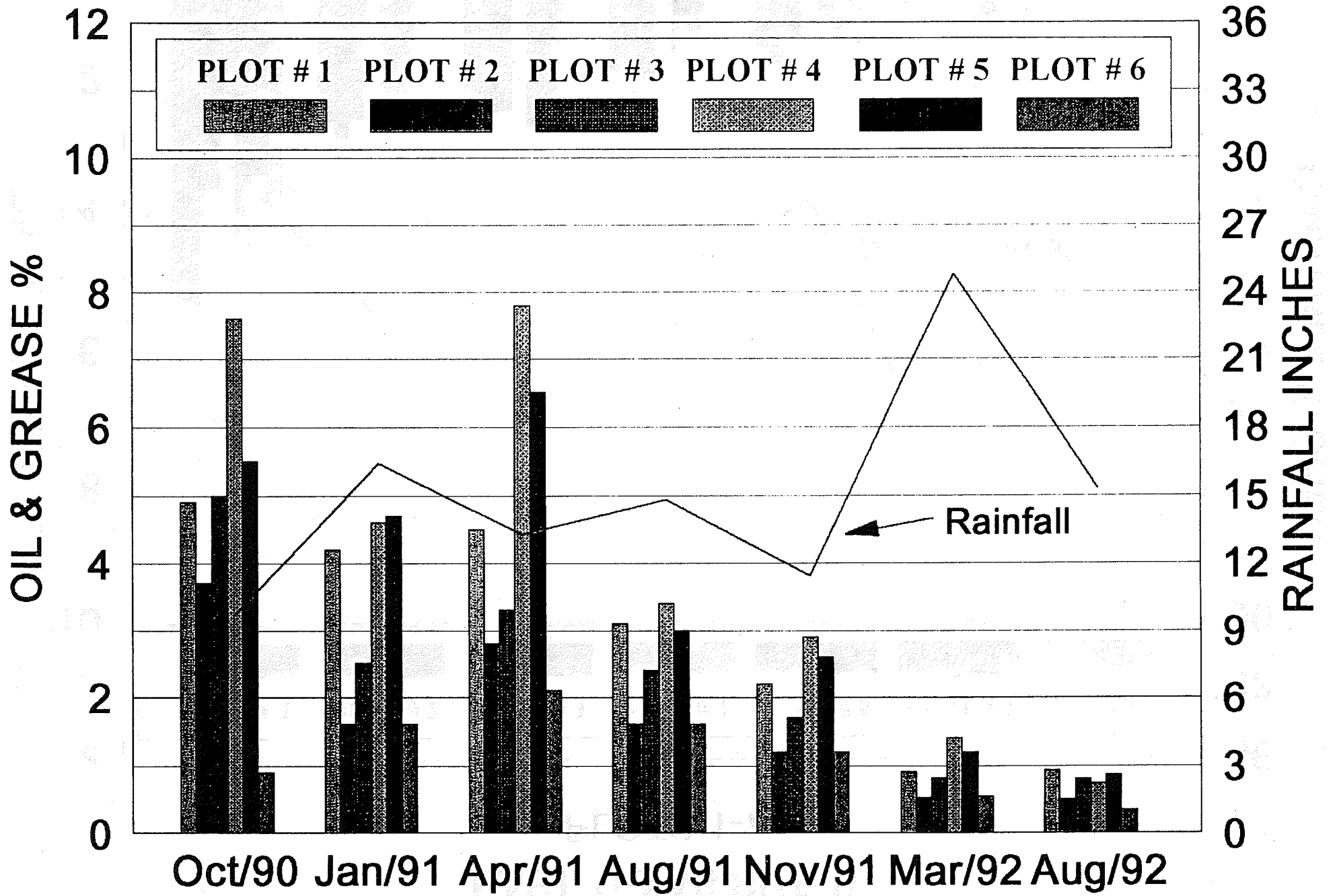
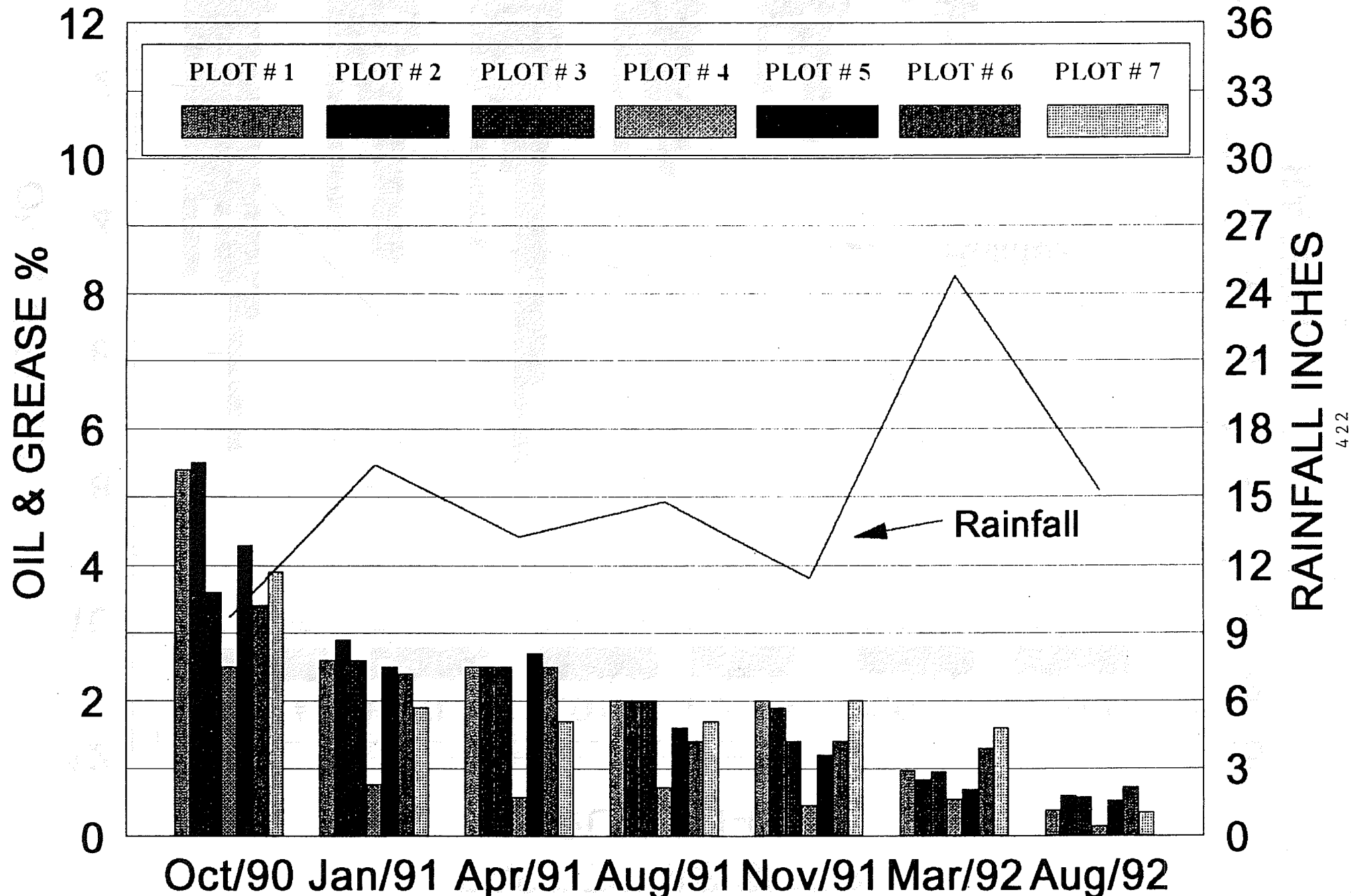
EAST TEXAS SITE A
PLOTS 1-6



EAST TEXAS SITE B
PLOTS 1-7



Practical Site Characterization for Oilfield Restoration

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Abstract:

Present oilfield economics dictate cost effective approaches to daily operations. With an ever increasing awareness of environmental issues and the public's opinion of the energy industry, exploration and production locations are subject to greater scrutiny by land owners and regulators charged with enforcing state laws dealing with oil and gas conservation and environmental compliance. Detailed evaluation for characterization of these sites is necessary for a successful cleanup following the commercial life of the property.

In order to understand physical parameters unique to each location for cleanup, the site must be properly characterized. Numerous issues and their relationship to each other must be addressed. An effective review and understanding of field conditions is used with any necessary data research to define possible limiting factors. Communication with land owners and regulators to meet any requirements or applicable standards must be a integral part of the process. Once properly identified, the relationship of all critical issues can aid in determining a cost effective solution for a successful location cleanup.

Introduction

The petroleum industry has experienced a significant reduction in profit margins in the past decade. With an increased public awareness of environmental issues and regulatory pressures, compliance at exploration and production sites to meet land owner wishes and state and federal regulations has reached a level requiring positive pro-active performance by operators. Marginal profit at the wellhead dictates a practical, hence cost effective, economic approach in dealing with environmental issues. As the final step in successful E & P activities, a location may require some restoration to enable the land owner to again realize fertility and consequently productivity on land previously used in E & P activities.

Present oil and gas field economics dictate a cost effective approach which takes into account daily operations and operating expenses. The operator must be aware of environmental issues which could impact any sites associated with E & P operations as well as any other production operations. As always, the knowledgeable operator must be ever cognizant of public opinion and how it influences the enforcement of existing laws and creation of new laws. With a greater scrutiny by land owners as well as regulators, the savvy operator must work within today's operating framework.

Acknowledgment

Acknowledgment is due the Oklahoma Energy Resources Board (OERB). The OERB is a state agency in Oklahoma which resulted from independent and major oil and gas operators supporting state legislation that created an agency charged by statute with two primary goals: to educate the public and clean up historic "oil field" sites. With over 550,000 wells having been drilled in the state in the past 100 years, there are a significant number of sites now abandoned and orphaned, with no responsible party that the Oklahoma Corporation Commission (OCC) can go to for any restoration activity.

Due to the large number of sites requiring restoration and logistics involved in managing such a program, it is necessary to utilize cost effective principals in the initial assessment of each project. While certain data research is necessary to fulfill due diligence requirements, field observations can and should be utilized in the Phase I assessment of each project. All too often, the day to day operations of carrying on the business of producing oil and gas doesn't allow us to "see the forest for

the trees". This paper will address those field observations that should enable operators and lease managers to "see the trees in the forest".

PHASE I Environmental Site Assessments

Any initial assessment of a site related to environmental issues is typically referred to as a Phase I Environmental Site Assessment (ESA). Formal Phase I ESAs for commercial properties grew out of legislation resulting in the "innocent land owner defense" under the Comprehensive Environmental Resource and Liability Act (CERCLA) passed by Congress in 1980. These Phase I ESAs have evolved as a means of protecting owners, operators and lending institutions from being in the "chain of title" and consequently assuming some potentially catastrophic economic liabilities. While there are certain guidelines defining site assessments for potential superfund sites under CERCLA, the requirements are so numerous and stringent as to make true CERCLA assessments extremely costly and impractical for the private sector.

There are currently no federal statutory definitions or standards of what should be included in a Phase I ESA. Several leading professional organizations have written guidelines for ESAs; one of the most widely accepted formats was written by the American Society for Testing and Materials (ASTM). This format defines Phase I ESAs but is still rather lengthy for petroleum extraction type sites and requires certain research that is not necessary for the vast majority of E & P work. Due to the nature of E & P sites, a traditional Phase I ESA normally associated with commercial/industrial properties is not applicable, but rather requires a modified assessment that primarily consists of a detailed site characterization.

In the first phase of a site review, or Phase I Environmental Site Assessment, (ESA), the primary objective is to gather information in order to determine whether or not the subject property has been or may be impacted by past and present on-site and off-site operations. Data research can include review of available literature, both for technical data as well as regulatory information which may pertain to the site.

A primary requirement during the Phase I assessment is the site visit, which includes a thorough physical on-site inspection, off-site review and owner interviews. Commercial properties evaluated for environmental parameters generally have a formal report prepared at the end of the assessment process. In the case of oil field operations, especially E & P sites, by knowledge of process we recognize the potential for impacting

air, soil and surface and ground water is already present. Consequently, our primary object should be to understand the physical characteristics of that site in order to negate or minimize potential impact and design a practical, cost effective restoration plan upon completion of the production activities at any E & P site.

As previously mentioned above, the primary interest in performing a site assessment is in properly characterizing the site by understanding the physical parameters. There are numerous issues to review in order to properly understand the relationship of each parameter. Limiting factors may include specific site conditions unique to a particular site and the availability of data necessary for further understanding the site itself. As always ,a critical component of successfully restoring any site to an acceptable level of "clean" is good communication with the land owner and any regulators that may be involved in the site restoration process.

Site Conditions

Site conditions can be determined by a number of cost effective means. The physical on-site visit can be yield field observations which can then be confirmed, if necessary, by data research. The nature of the constituents is available by knowledge of process of E& P sites, i.e., we know we are dealing with liquid hydrocarbons, either crude oil or condensate, produced formation water, lease chemicals and lubricating oils and grease as may be required on-site. Sampling and testing can be limited or as may be necessary to meet regulatory requirements. Evaluation of migratory pathways for any produced liquids or lease chemicals and available receptors must be evaluated in order to determine impact of spills and accumulated leaks, drips and drops. Finally, communication must continue to maintain a working relationship with all involved parties.

Surface Water

One of the primary considerations in any site characterization involves the protection of surface as well as ground water. Many of the federal laws that impact the petroleum industry are directed at protecting water. While this may involve substantial compliance at some sites, a practical evaluation of proximity to any water is necessary to thoroughly understand the site and insure protection of these valuable resources. Field observations should include whether the site in question is in proximity to streams and whether those near-by streams are permanent

or intermittent, presence of ponds and lakes and intended uses of these bodies of water, and whether or not there are any watercourses that may become a flowing body of water during storm events which typically produce overland flow. Direction and distance to these bodies of water should always be noted.

Field observations may be confirmed by data research involving use of United States Geological Survey (USGS) topographic maps, aerial photos, both past and present and flood plain maps published by the Federal Emergency Management Administration (FEMA). Flood plain maps are usually available for review at county soil or agriculture extension offices and may also available at insurance agencies and libraries.

Ground Water

Ground water is a receptor that must be evaluated carefully as any impact can cause the operator concern and substantial economic impact for restoration. Field observations include the presence and proximity to permanent streams, ponds, lakes and water supply wells. The presence of any water well in close proximity must be noted as to distance to the site, depth, water quality and flow or pump rates.

Data to be researched includes information readily available from state geological surveys, state water resources agencies, and especially state oil and gas regulatory agencies or departments. Some of the most significant resources available to the operator are interviews with the land owner and adjacent parties. Often their farming and ranching success is dependent on knowledge of available sub-surface water, water quality and well flow rates. Together these resources can provide a detailed account of ground water quality and availability.

Soil

As we can readily observe, any spill, whether a small or large volume, will first impact the soil prior to any damage to surface or ground water. Soil is a complex and varied subject which represents an entire body of scientific data and knowledge. In the scope of this presentation, we will consider only two types of soil. As an operator, we need to be primarily concerned with whether the soil is sandy or clayey. Sandy soils tend to allow liquids to penetrate while clayey soils tend to allow liquid spills, leaks and drops to accumulate on the surface. Field observations

include road cuts, ditches, plowed fields, graded locations and vegetation types.

Data research includes review of soil surveys available at United States Department of Agriculture, Natural Resource Conservation Service (USDA SRCS) county offices and state agriculture extension offices associated with various state soil conservation programs. Other considerations that should be observed in the field include soil permeability, or how fast liquids soak into the soil, and slope, which provides run-off during vessel failure or other catastrophic events. Resource personnel available to interpret site specific soil and soil conditions include federal and county agronomists and soil scientists.

Other Factors

Two primary factors that may need to be considered when characterizing a site include depth to bedrock and proximity to wetlands. Depth to bedrock can be confirmed by field observations which include outcrops in road cuts, ditches, fields and graded areas. Additional information which can be acquired by data research is available from state and federal geological surveys and some state oil and gas agencies.

Proximity to wetlands can be determined by field observations which include location of natural springs, seeps, vegetation types and soil type. Data research for wetlands determination can be completed from the United States Department of the Interior, Fish and Wildlife Department, the United States Environmental Protection Agency, the United States Department of Agriculture, and the United States Army, Corps of Engineers. The most readily available source is the USDI, Fish and Wildlife Department wetlands maps, which were created as part of a national wetlands study and are usually available from various state or federal agencies.

Additional factors that may require consideration during site characterization include whether the site is in a hydrologically sensitive area, whether the site is in a well-head protection area and what the intended land use, both historical and present day, is for the site/property. Field observations would include proximity to stream and terrace deposits and depth to shallow ground water. Data resource sources would include information from state oil and gas agencies, state water resource agencies and federal data bases.

Land Use and Site Specific Hazards

In order to properly determine restoration goals during the site characterization, historical and present land uses must be considered. In rural settings, the site must be evaluated as to intended uses for cultivated or pasture areas, return to native vegetation, impact on any rural residents or if the area has been or may be used as a recreational area. In populated areas or municipalities, land uses that should be considered include location on the municipal fringe or edge of town, areas that may have been used for industrial or commercial ventures, whether the site is in or near residential areas, and whether the site has been or may be used as a city park or in another recreational type setting.

There are certain site specific hazards that should be noted, as much to protect the investigator as to note conditions that may hamper or restrict restoration activities. Insects, reptiles, limiting physical conditions, site size and physical layout should be noted to inform future personnel that may be associated with restoration activities. Communication, whether written or verbal, is as important as the physical state of the site when it comes to safety.

Contaminant Constituents

As previously mentioned, primary constituents of concern that may impact the site include crude oil or natural gas condensate and produced formation water. The major constituent of produced water that causes the greatest challenge in site restoration is chlorides, although sodium can cause issues in soil restoration as well. Other constituents of concern to note as present at a site include refined products, lease chemicals, heavy metals that may be present due to drilling mud chemicals, general E & P wastes and miscellaneous trash and debris. Finally, Naturally Occurring Radioactive Materials (NORM) should be noted in the event it is present due to produced liquids that may carry radionuclides in the production process.

Contaminant Sources

Contaminant sources must be evaluated to confirm potential volumes and presence of potentially impacted areas around a site. Small volume point sources are cumulative over time. A point source will typically produce a small volume which can create a cumulative effect over a number of years and usually results from leaks, drips and drops.

Typical point sources may include loose fittings, poor connections, corroded equipment, small flow line breaks, and improperly or incompletely closed valves, just to name a few.

Large volume point sources may result from catastrophic events that produce a single event occurrence. Line breaks, tank overflows, vessel failures and lightening strikes are some examples of petroleum operations disasters that can cause a major impact to the environment. Field observations will result in reduced impact if attention to small details around the site result in "good housekeeping".

Pathways

The medium through which E & P contaminants must move in order to reach target receptors is generally the same in both rural and municipality settings. Open tanks and hatches, accumulated leaks, drips and drops, and spills of varying sizes will initially enter the air and soil. Lighter ends will volatilize and the heavier ends will then subject soils to accumulated concentrations. If the point source is allowed to continue to contribute contaminants to the environment, then the soil becomes the medium or pathway as the contaminant is transported to surface water and/or ground water. Principal pathways include soil, surface and ground water, which can transport constituents to livestock, pets, cultivated lands, gardens, recreational areas, and ultimately, humans.

Receptors

Receptors must be evaluated to define impact of operations from any leaks or spills that may occur during the life of the property. Necessary restoration activities must take into account site location and nature of potential receptors.

Typical rural locations provide unlimited access as around the clock security is generally not feasible. Potential receptors that may be impacted include soil, air, surface water, ground water, livestock, crops and humans. Typical locations in municipalities generally have limited access due to fencing, alarms, and marginal security. Receptors associated with operations near municipalities that may be impacted include soil, air, surface water, ground water, pets, lawns and gardens and humans. In both settings, field observations and prompt response to an event will minimize both impacted receptors and restoration costs.

In-house Data

Often costs of acquiring data to aid in detail research, although small in incremental amounts; can be cumulative over a number of sites and consequently cost prohibitive to many operators. Field observations offered in this presentation can be supplemented by data that is more than likely already in hand for many oil and gas operators. Prospect, land and well files may include such data resources as topographic maps, geologic outcrop and/or subcrop maps and aerial photos, either recent or historical.

Data research for past and present land uses and ownership may also be available for review from various land files. There is available data associated with normal exploration and production operations that we need to review before the purchase of data that well may be duplicative in nature and already in hand.

Site Influences

Considerations in practical site characterization also include certain influences that may define how much detail is necessary to properly review all parameters of a site. Timing to restore the site is a critical parameter in creating a restoration plan. Obviously, a longer time period, if available, will allow the sequence of events to progress in nature's time. Proximity to humans, residents, or livestock may play a critical role in influencing how much detail is necessary in characterizing a site for restoration. Certainly, land owner wishes and any regulatory pressure may well require the most consideration in how much detail is necessary and how any site is restored. These influences are primary to a successful site restoration.

Conclusion

In conclusion, sound field observations can replace a significant amount of data research for a practical site characterization. When necessary, there is a large amount of technical data readily available from public, state and federal data bases at a reasonable cost to supplement field observations as required. By our knowledge of process, knowledge of operations and knowledge of the chemical constituents that we are most likely to encounter on an E & P site, we should be able to determine pathways and impact on any potential receptors. With limited sampling and testing, constituent concentrations and extent can be defined. By

maintaining good communications with land owners, regulatory personnel and the community, if necessary, site characterization and restoration will be cost effective and successful.

The Utilization of Combined Gas Chromatography-Isotope Ratio Mass Spectrometry to Monitor the Origin and Fate of Crude Oil Spills in the Environment

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ABSTRACT

Gas chromatography-isotope ratio mass spectrometry (GCIRMS) has rapidly gained acceptance as an additional powerful and complimentary correlation tool to gas chromatography (GC) and gas chromatography-mass spectrometry (GCMS). GCIRMS permits one to determine the isotopic composition of individual compounds in complex mixtures rather than only being able to utilize bulk isotopic compositions of whole oils or fractions such as saturates and aromatics. This paper discusses the application of GCIRMS to a variety of problems associated with petroleum spills in the environment. Because of the nature of this presentation the emphasis will be placed on use of GCIRMS.

When an oil or refined product is spilled into the environment, weathering will start immediately. Evaporation, water-washing will be quickly followed by the onset of biodegradation. All of these processes quickly change the fingerprint of the original product that was spilled making it difficult in certain cases to undertake correlation studies. This uncertainty in the ability to correlate becomes a major problem in an environmental sense where such factors are important in the determination of who was responsible for the spill and more importantly who is responsible for cleaning up the residue. The origin of the spills may be supertankers on the oceans, crude oil or natural gas pipelines or underground storage tanks at the corner gas store. Examples are presented utilizing samples derived from all of these sources to demonstrate how it is possible to correlate spills with their sources even if extensive weathering has occurred making it difficult to correlate using conventional techniques. GCIRMS will have a very important role to play in many environmental areas, and when used in conjunction with the other analytical techniques will raise our ability to pin-point sources of spills to a much higher level. The ability to correlate unweathered and weathered samples, whether oils or refined products, will be a particularly important aspect of this technique.

INTRODUCTION

The types of organic compounds spilled into the environment, either accidentally or intentionally, are many and varied and may range from pesticides to chlorinated solvents to toxic warfare reagents to crude oils and refined petroleum products. There is an on-going interest to improve our ability to correlate such pollutants with their source(s). The present paper is specifically concerned with hydrocarbon products spilled into the environment and the development of a relatively novel analytical approach, gas chromatography-isotope ratio mass spectrometry (GCIRMS), which can be used, in conjunction with other techniques, to undertake correlations and determination of the source for such spills. It should be noted that GCIRMS will be equally applicable for other types of chemicals spilled into the environment. Naturally each class of compounds will react in a different way once it is spilled in the environment. From the moment a hydrocarbon spill occurs the composition of the spilled product will start to change. Initially the changes will be dominated by evaporation and water washing, both of which tend to remove the lighter hydrocarbon components in the oil (1). Within a relatively short period of time, biodegradation will become dominant and then not only will the residual light components be removed, but progressively heavier components are also removed in a fairly specific and predictable manner (2). Ultimately all of the saturate hydrocarbons will be removed leaving an unresolved complex mixture of components that are very resistant to biodegradation. With this scenario in mind it becomes extremely difficult to undertake correlations between unaltered and altered samples. Techniques such as gas chromatography (GC) or gas chromatography-mass spectrometry (GCMS) have been used to obtain fingerprints of various compounds classes for correlation purposes (3). Two samples coming from the same source, or which are genetically related to each other, may be expected to have the same fingerprint but once the fingerprint has been altered as result of weathering it becomes difficult to undertake correlations with any degree of confidence.

Recent advances have lead to the development of gas chromatograph-isotope ratio mass spectrometry (GCIRMS), which appears to be a potentially powerful correlation tool (4-7). GCIRMS in effect provides the ability to determine the isotopic composition of individual components present in complex mixtures which are resolvable by gas chromatography. Prior to this development, use of carbon isotopic values was limited to determination of bulk isotopic values for unfractionated samples or individual fractions such as total saturate, aromatic, or polar fractions of crude oils (8,9).

The purpose of this paper is to illustrate the role of GCIRMS in the correlation of hydrocarbons, which are contaminants in the environment, with their suspected sources. The basic premise being that as long as individual components, such as n-alkanes, can be detected in the weathered samples, the isotopic composition of these individual components in unweathered and weathered samples should be virtually identical.

In the following section, examples of this technique will be discussed along with its application to the correlation of several weathered and unweathered samples. It will be shown also that this approach can be used to detect the source of hydrocarbons responsible for the oiling of birds in an area affected by a spill. Finally it will be demonstrated that in heavily biodegraded oil, an asphaltene fraction may be isolated and the asphaltenes pyrolysed and the isotopic compositions of the resulting pyrolysis products used for correlation purposes.

EXPERIMENTAL

Samples

For the purposes of this study, samples of crude oils, fuel oils, gasoline samples and tar balls were obtained from a variety of sources. Specific locations of samples will not be given since they are not necessary for the discussion. Samples were obtained in both unweathered and weathered condition. In some cases the samples were weathered naturally and in other cases the samples were weathered artificially in the laboratory.

Gas Chromatography

Prior to analyses by GCIRMS the samples were analysed by gas chromatography. For the most part the samples were typically analysed, without any fractionation, using a DB-1 fused silica capillary column (0.25mm i.d.; 1.0μm film thickness) and temperature programmed from 40 to 300°C at 4°C/min.

Gas Chromatography-Mass Spectrometry

To provide the additional data needed for correlation purposes, samples were analysed by GCMS using a Finnigan TSQ 70 combined with a Varian 3400 GC. Temperature conditions were the same as described above and the system was normally used in the GCMS mode monitoring commonly used biomarker ions such as m/z 191 and m/z 217 for determination of terpane and steranes respectively.

Gas Chromatography-Isotope Ratio Mass Spectrometry

The GC-IRMS analysis were performed using a Finnigan MAT 252 Isotope Ratio Mass Spectrometer coupled with a Varian 3400 gas chromatograph. Most of the samples were analyzed with a DB-1 fused silica capillary column (0.32mm i.d.; 0.25μm film thickness ; 60 m) and temperature-programmed from 40 to 300°C at 2°C/min. Most of the samples were fractionated by HPLC or liquid chromatography prior to GC-IRMS analysis in order to analyze only the saturate fractions and simplify the chromatography.

RESULTS AND DISCUSSION

Crude oils, and refined petroleum products, are very complex mixtures of a wide variety of compound classes, including saturate, aromatic, and polar compounds. Oils can be fractionated into the compound classes by a variety of chromatographic techniques, such as HPLC, column chromatography, or thin layer chromatography. It should be noted that in all of the analyses described herein deuterated hydrocarbon standards of known isotopic compositions are included with each sample to check reproducibility of the system.

In a previous paper we have demonstrated many of the basic concepts of this approach using a variety of weathered and unweathered samples. In this study we wish to concentrate more on the laboratory studies designed to simulate weathering processes and furthermore demonstrate that the GCIRMS approach will work with weathered samples. One example, taken from our earlier study is shown in Fig. 1, demonstrates the relationship between a weathered and unweathered fuel oil sample, neither of which contains any of the conventional biomarkers and so requires an alternative approach, such as GCIRMS, for correlation purposes.

To determine whether or not weathering processes can compromise any correlations between pollutants and suspected sources, an initial experiment was performed using an oil that had been allowed to evaporate over a four year period in the laboratory. Aliquots of the original oil were also water-washed (a mixture of about 100 ml of oil and 800 ml of distilled water stirred in a beaker for 2 months) and artificially biodegraded (Fig. 2). The evaporation process is marked by the loss of n-alkanes below C_{14} and after 38 days, the water-washed oil is notably depleted in n-alkanes below C_{15}. The iso- and cyclo-alkanes eluting before the n-C_{15} have also been partially or totally removed. The aromatic fraction is more affected by the water-washing because of the higher aqueous solubility of aromatic compounds. These experimental results are consistent with those previously reported in the literature (10). After 1 month, the biodegraded oil was

depleted in lower molecular weight n-alkanes but the pristane/C_{17} and phytane/C_{18} ratios were not affected by biodegradation. The predominance of the n-C_{25}-C_{35} alkanes was unexpected and may result from an increase in the relative concentration of these compounds as a result of: (i)the biodegradation process; (ii)contamination; (iii)loss of the components below n-C_{25} during the analytical process. The third hypothesis is unrealistic and would only account only for loss of hydrocarbons below n-C_{17}. The second hypothesis can also be discarded since the isotopic composition of the high molecular weight components is very consistent with the isotopic composition of the same compounds in the non-biodegraded oil whereas any contaminant would have shown different values. After 2 months of biodegradation, the n-alkanes were severely affected by biodegradation, their relative concentrations severely reduced, and the pristane/C_{17} and phytane/C_{18} ratios have increased because of the removal of the n-alkanes. After four months, the n-alkanes have been completely removed and only a few iso-, cyclo-alkanes and some biomarkers can still be identified.

The isotopic composition of individual n-alkanes of these three artificially weathered oils have been determined and compared to those of the initial oil (Fig. 3). Despite the partial loss of n-alkanes below n-C_{15}, a good correlation exists between the evaporated, water-washed and unweathered oils (Figs. 3a and b). The deviation between the isotopic values of the weathered and unweathered oils remains within the analytical error except for a few peaks affected by a high background or coelutions. After one month the biodegraded oil shows a slightly enriched ^{13}C isotopic composition (Fig. 3c) probably due to the high background resulting from the hump induced by the biodegradation rather than to an isotopic fractionation resulting from the biodegradation. In order to eliminate the coelution problems, the saturates from the oil that had been biodegraded for two months, was further fractionated into linear and iso-, cyclo- alkanes and the linear fraction analyzed by GC-IRMS. The isotopic values of the linear fractions of the biodegraded and initial oils showed a very close correlation. The lack of n-alkanes in the oil that had been biodegraded for four months prevented any GC-IRMS analysis of the saturate fraction. However, a new approach for the analysis of severely biodegraded is proposed in the following paragraphs. These first results demonstrate that the weathering does not affect the isotopic composition of individual components of an oil as long as individual components can be identified.

Following the laboratory observations, examples of natural weathering processes resulting from actual spills in the environment were investigated. The first example involves a flock of birds that were killed as a result of an oil spill and which had washed up onto a beach. In order to try and determine the origin of this oil, the bird feathers were extracted and the extracted oil compared to several suspected sources. GC and GC-MS analyses permitted several of the

suspected sources to be discarded and eventually a light fuel oil was selected as the major suspect for the source. Correlation of the two samples purely on the basis of GC and GC-MS were inconclusive since the oil from the bird feathers was weathered and both oils had the characteristics of a light fuel marked by the absence of biomarkers (Figs. 4a and b). Thus, the oils were analyzed by GC-IRMS and comparison of their isotopic values demonstrated their similarity. The two distributions show very close trends and the deviation does not exceed the range of the analytical error for most of the n-alkanes (Fig. 4c). On the basis of these data it was therefore proposed that the birds had been killed as a result of coming into contact with a light fuel oil from a tanker that had run aground in the area.

In general, the correlation of light fuel oils, or refined products, to their suspected sources remains difficult using conventional methods. The absence of biomarkers and the weathering that removes the light ends typically prevent any successful correlation on the basis of GC and GCMS analysis. However, the use of GC-IRMS in these situations will provide an alternative method for the correlations.

The second example deals with moderately to severely biodegraded crude oils in the form of tar balls which had been extensively weathered by evaporation, water washing, and biodegradation. Hydrocarbons from these tar balls have been characterized by high temperature gas chromatography (11; Fig. 5). As observed in the laboratory biodegradation experiments described above, the hydrocarbon fractions are dominated by the longer chain n-alkanes, typically above C_{30}.

GCIRMS analysis of the saturate fractions confirmed the results of GC-MS analysis (Fig. 6) and the dissimilarities observed between 94F and 95F (more than 2 ‰ for most of the isotopic values of the n-alkanes) are attributed to a different origin (source and/or facies) rather than to variations in the extent of biodegradation of the two samples. The isotopic compositions of n-alkanes in samples 95M and 95H are quite similar and suggest a common origin for these two samples but the deviation between the two samples is often over the range of the analytical error. So, there was still some ambiguity regarding the relationship between these two samples. Because of the extensive biodegradation of samples 95M and 95H, GC-IRMS data were only obtained on a limited range of n-alkanes (C_{32}-C_{40}) and these compounds also elute in a region of the chromatogram where the background is quite high which may affect the accuracy of the isotopic data.

In view of these potential problems and limitations, an alternative method has been investigated for the characterization of these samples. It has been previously observed that asphaltenes have a similar, but less condensed, structure than the kerogen from which they originate (12). Studies have shown that the

aliphatic moieties bound into the asphaltene structures are not altered by the biodegradation processes and therefore hydrocarbons generated by pyrolysis of the asphaltenes from biodegraded and non-biodegraded oils show very similar distributions of n-hydrocarbons. This technique has been applied with some degree of success to the correlation of degraded and nondegraded oils. These correlations are generally undertaken on the basis of the n-alkene/n-alkane doublet distributions. Considering that pyrolysis of asphaltenes regenerates individual components, analysis of the pyrolysis products by GCIRMS should provide an additional and more specific means of correlating degraded and nondegraded samples.

In order to investigate the correlation potential of pyrolysis combined with GCIRMS, the asphaltenes of the four tar balls described above were isolated and pyrolyzed at 800°C for 20 ms. The saturate fractions of the pyrolyzates were analyzed by GCIRMS (Figs. 7 and 8) and the results confirm the proposed similarity between samples 95H and 95F as defined previously by GCMS and GCIRMS analysis of the saturate fraction. The deviation of the isotopic values between the two samples is quite high (about 1 ‰) but the trends are very close throughout the range C_{13}-C_{35}. These deviations can be rationalized by coelution problems induced by the complexity of the pyrolysates, including the n-alkene/n-alkane doublets. The very different trends and the high deviation of the isotopic values (between 2 and 3 ‰) obtained from samples 95F and 94F confirm the previously proposed hypothesis of their different origins.

This example demonstrates how a combination of different analytical techniques can be useful in drawing precise conclusions regarding the correlation of biodegraded oils. Furthermore it illustrates that GCIRMS is not limited to only slightly or moderately weathered oils, which still contain identifiable individual components, but has the potential to be extended to extensively degraded samples with no resolvable components.

These results suggest that GC-IRMS has the potential to become a powerful tool for correlation of weathered and unweathered oils spilled in the environment. Thus, when a spilled oil has lost its main characteristics (light hydrocarbons for the gasolines or most of its individual components when a crude oil is severely biodegraded), GC-IRMS can provide an alternative approach, supplementing data from conventional methods.

SUMMARY

The purpose of this paper has been to introduce the concept of GCIRMS as a potential monitoring and correlation tool for use in a variety of environmental problems. The examples used in this particular study are related to environmental problems caused by contamination from crude oils or refined hydrocarbon products. It is proposed that ultimately the technique can be used for other environmental problems. It is not suggested that GCIRMS should be used as a stand-alone technique. Rather it raises the degree of confidence to which correlations are made to a higher level than those simply based on GC and GCMS data. This is particularly important when the samples being examined are weathered or heavily biodegraded. The successful use of GCIRMS depends on the premise that with weathering and biodegradation, the isotopic composition of individual components in a mixture will not be greatly affected. Hence as long as individual components remain in the weathered sample then isotopic compositions can be determined and used for correlation purposes.

With very heavily weathered samples, the aromatic fractions may be utilized for correlation purposes since these components are more resistant to biodegradation. However a potential problem with the aromatic fractions is their great complexity and the need for good resolution of individual components in order to obtain reliable isotopic data. This problem can be rectified to a large extent by additional fractionation of the aromatic fraction since it is already known that such fractionation will not affect the isotopic compositions of the individual components.

In brief GCIRMS has the potential to become a very powerful correlation tool to be of use in environmental problems. It will be of most use when used in conjunction with other analytical techniques such as GC or GCMS. It will be of greatest additional value in the cases of samples that are heavily biodegraded to the extent where changes have started to occur to the biomarker distributions making correlations difficult or impossible by conventional techniques.

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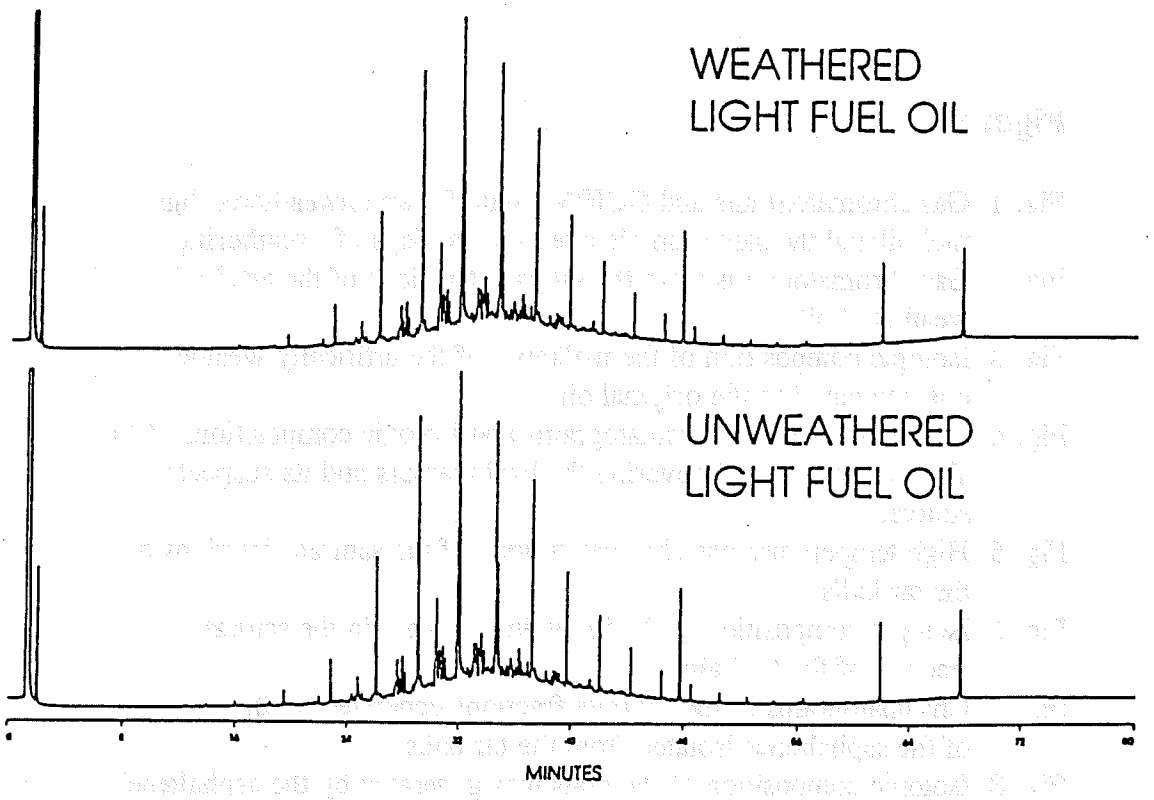
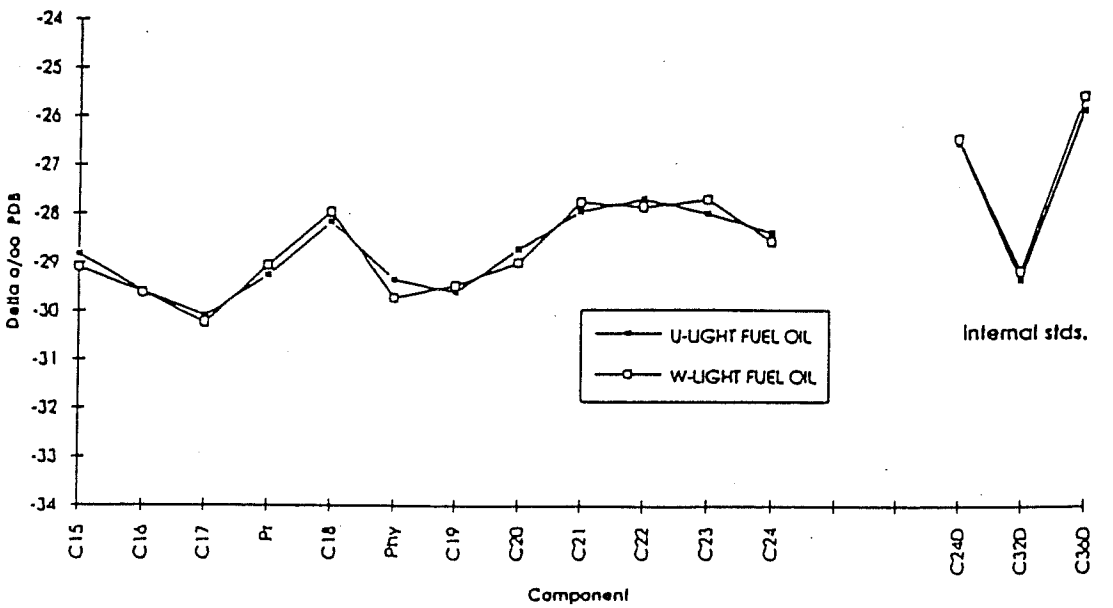
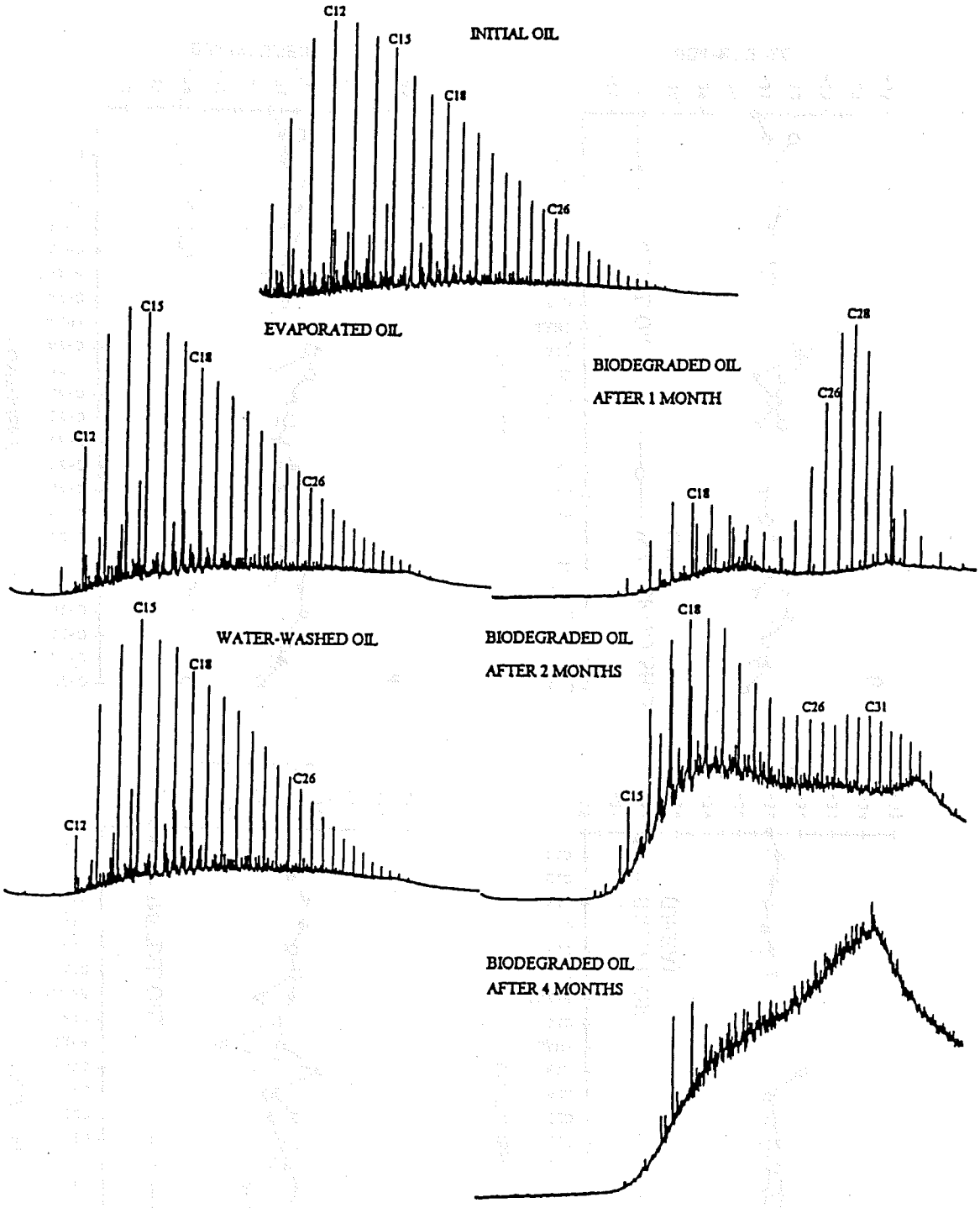
Figures

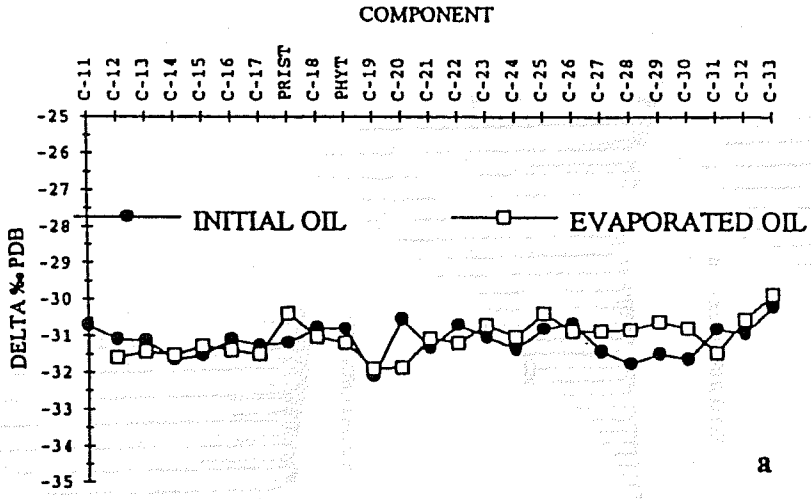
Fig. 1 Gas chromatograms and GCIRMS data for an unweathered light fuel oil and the same sample after several days of weathering.
Fig. 2 Gas chromatograms from the saturate fractions of the artifically weathered oils.
Fig. 3 Isotopic composition of the n-alkanes of the artifically weathered oils compared to the original oil.
Fig. 4 Comparison of the chromatograms and isotopic compositions of the alkanes from the oil covering the bird feathers and its suspected source.
Fig. 5 High temperature gas chromatography of the saturate fractions of the tar balls.
Fig. 6 Isotopic composition of the individual alkanes in the saturate fraction of the tar balls.
Fig. 7 Chromatograms of the saturate fractions generated by the pyrolysis of the asphaltenes isolated from the tar balls.
Fig. 8 Isotopic composition of the n-alkanes generated by the asphaltene pyrolysis of the tar balls.

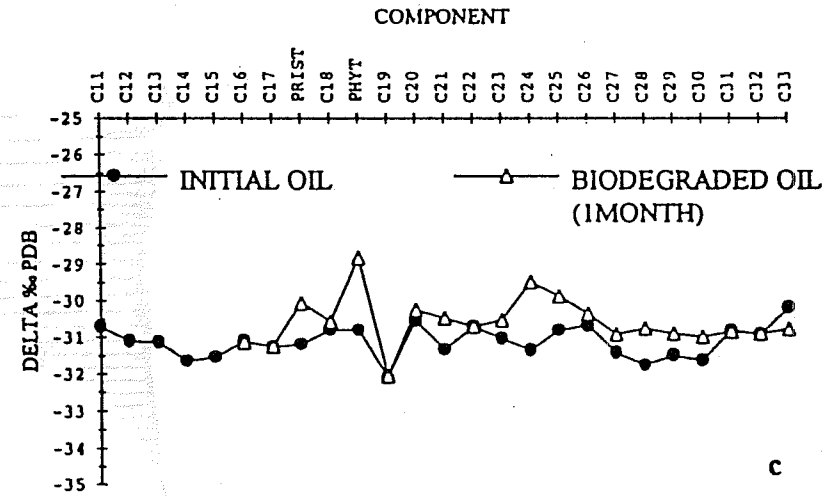


GCIRMS - Unweathered vs. Weathered Fuel Oil




C12
C15
INITIAL OIL
C18
C26
EVAPORATED OIL
C15
C18
C12
C26
BIODEGRADED OIL
AFTER 1 MONTH
C28
C26
C18
C15
WATER-WASHED OIL
C18
C26
C12
BIODEGRADED OIL
AFTER 2 MONTHS
C18
C26
C31
C15
BIODEGRADED OIL
AFTER 4 MONTHS


COMPONENT
C-11 C-12 C-13 C-14 C-15 C-16 C-17 PRIST C-18 PHYT C-19 C-20 C-21 C-22 C-23 C-24 C-25 C-26 C-27 C-28 C-29 C-30 C-31 C-32 C-33
DELTA ‰ PDB
-25 -26 -27 -28 -29 -30 -31 -32 -33 -34 -35
INITIAL OIL
EVAPORATED OIL
a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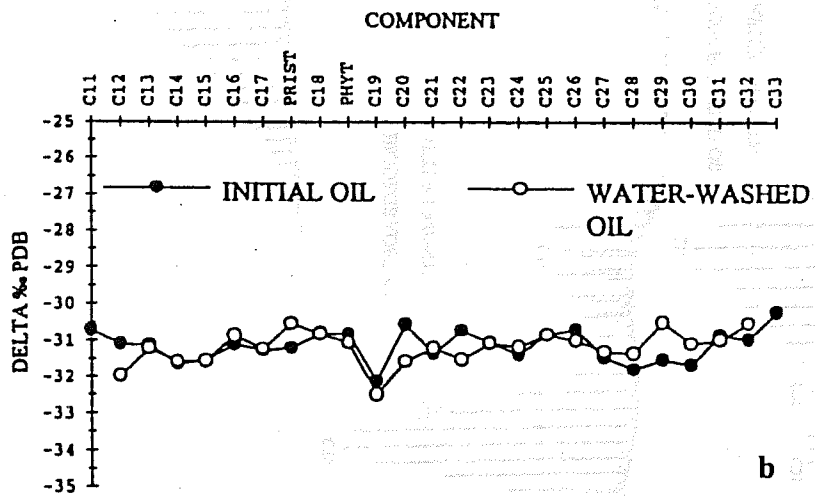
DELTA ‰ PDB
-25 -26 -27 -28 -29 -30 -31 -32 -33 -34 -35
INITIAL OIL
BIODEGRADED OIL
(1MONTH)
c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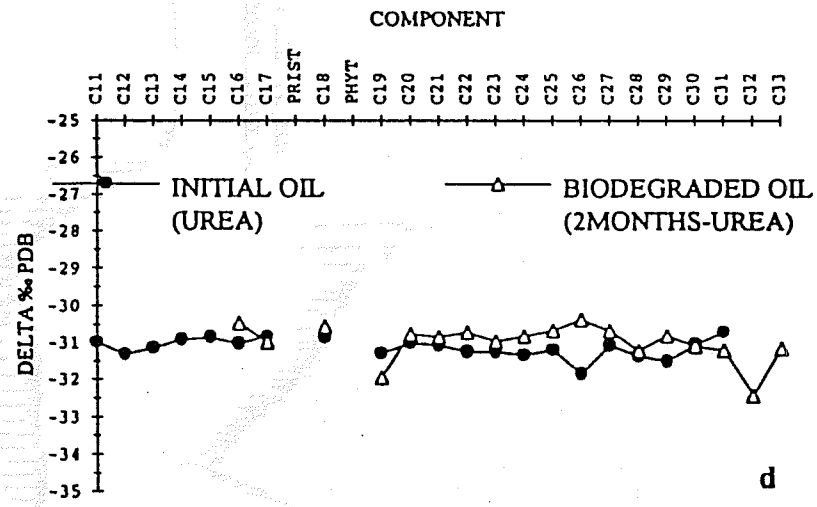
-25 -26 -27 -28 -29 -30 -31 -32 -33 -34 -35
INITIAL OIL
WATER-WASHED
OIL
b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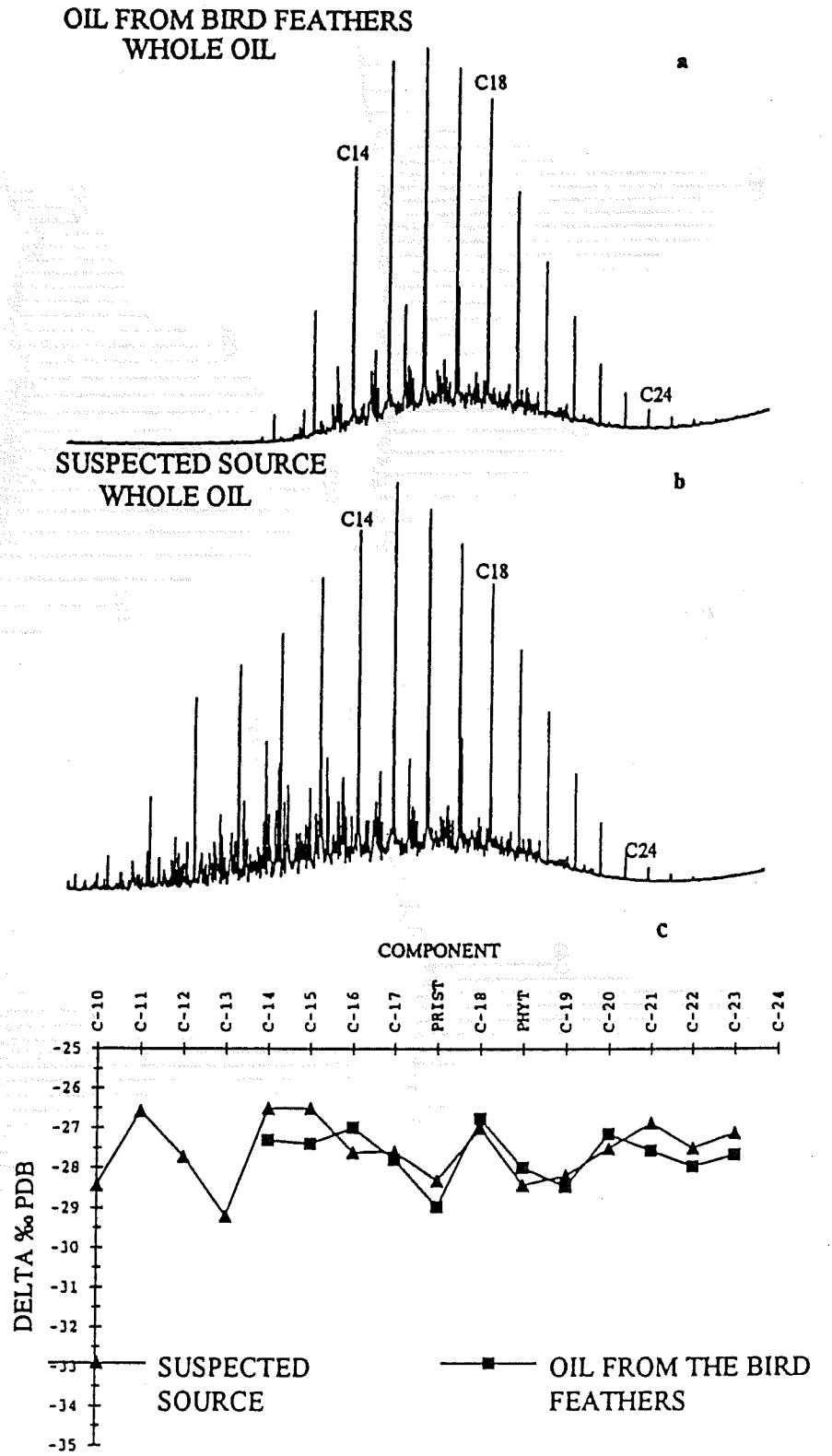
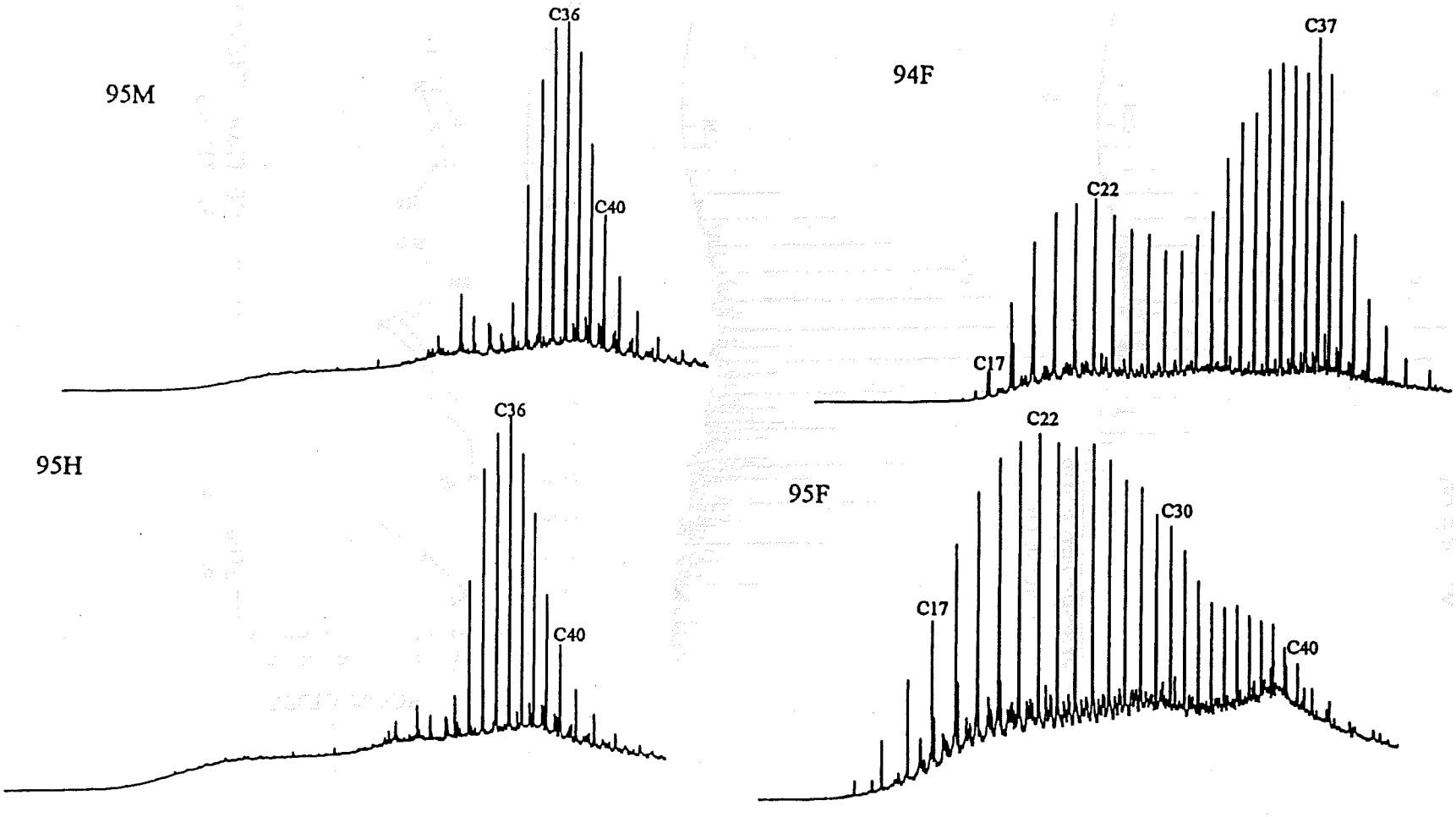
DELTA ‰ PDB
-25 -26 -27 -28 -29 -30 -31 -32 -33 -34 -35
INITIAL OIL
(UREA)
BIODEGRADED OIL
(2MONTHS-UREA)
d


OIL FROM BIRD FEATHERS
WHOLE OIL
a
C14
C18
C24
SUSPECTED SOURCE
WHOLE OIL
b
C14
C18
C24
c
COMPONENT
C-10
C-11
C-12
C-13
C-14
C-15
C-16
C-17
PRIST
C-18
PHYT
C-19
C-20
C-21
C-22
C-23
C-24
-25
-26
-27
-28
-29
-30
-31
-32
-34
-35
DELTA ‰ PDB
SUSPECTED SOURCE
OIL FROM THE BIRD FEATHERS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C36
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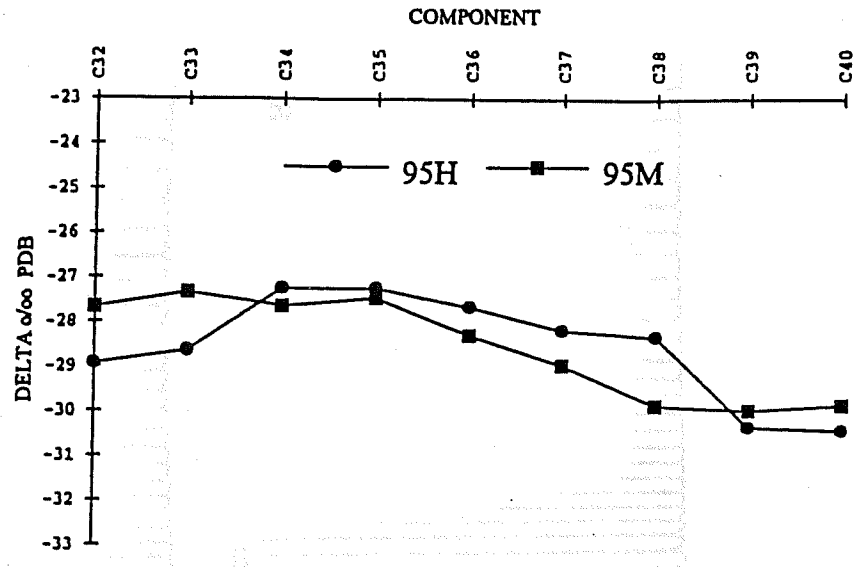
94F
C37
C22
C17
95H
C36
C40
95F
C22
C30
C17
C40


COMPONENT
C32
C33
C34
C35
C36
C37
C38
C39
C40
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-26
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-30
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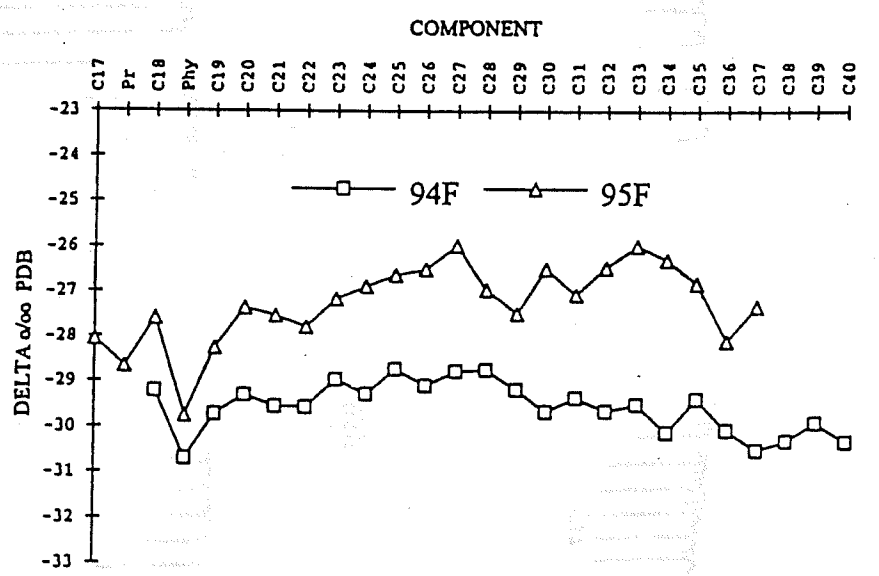
-33
95H
95M
DELTA o/oo PDB


COMPONENT
C17
Pr
C18
Phy
C19
C20
C21
C22
C23
C24
C25
C26
C27
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C30
C31
C32
C33
C34
C35
C36
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C38
C39
C40
-23
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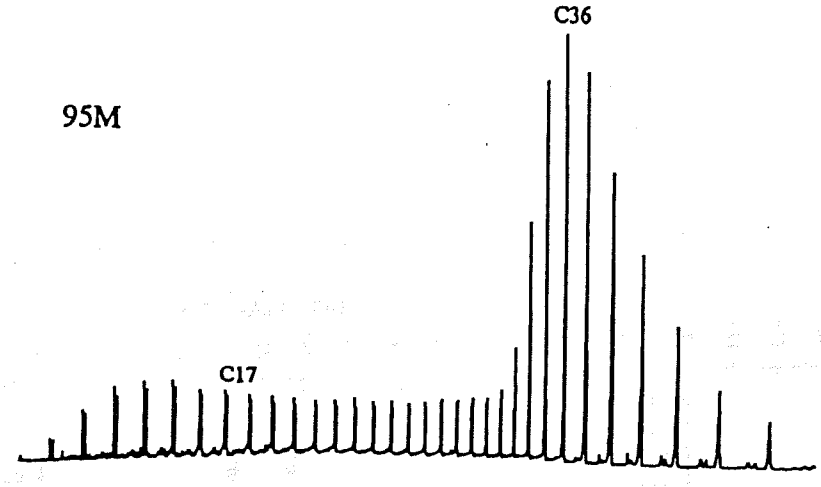
-30
-31
-32
-33
94F
95F
DELTA o/oo PDB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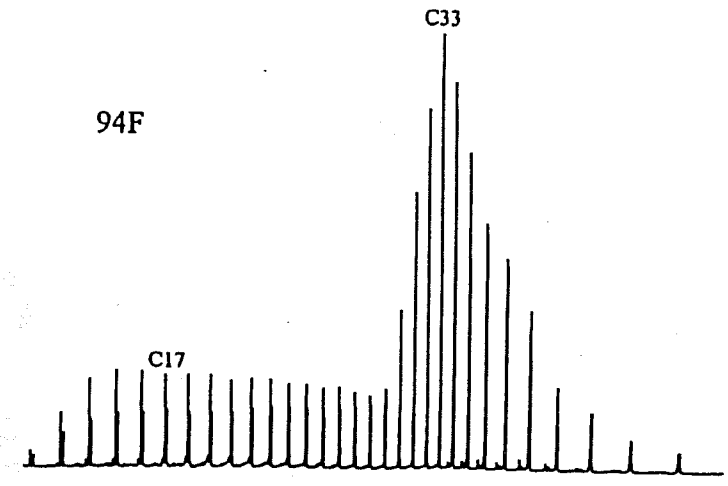
C36
C17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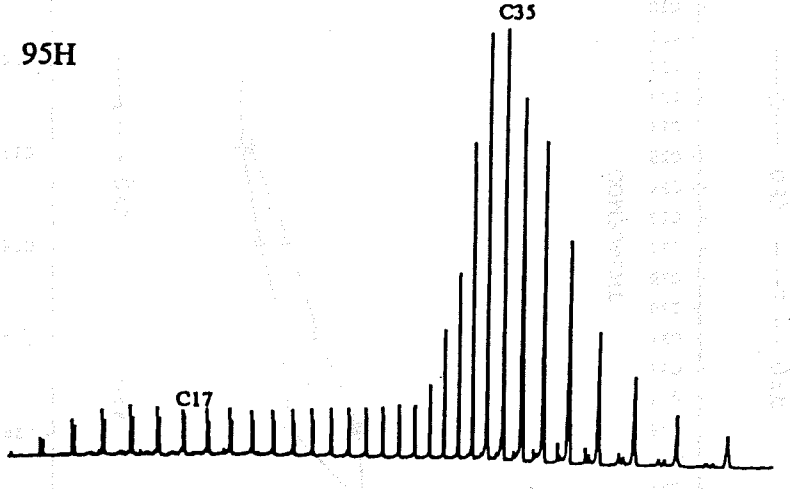
C33
C17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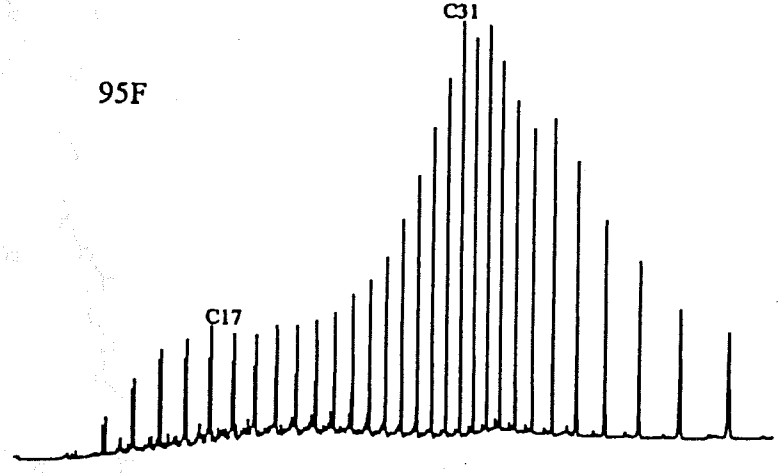
C35
C17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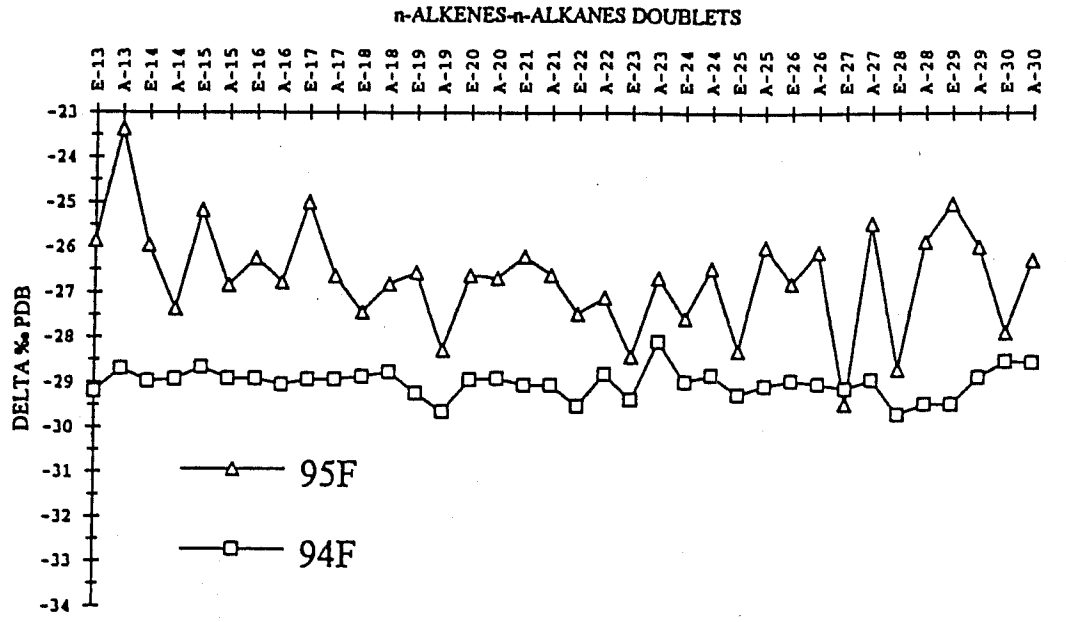
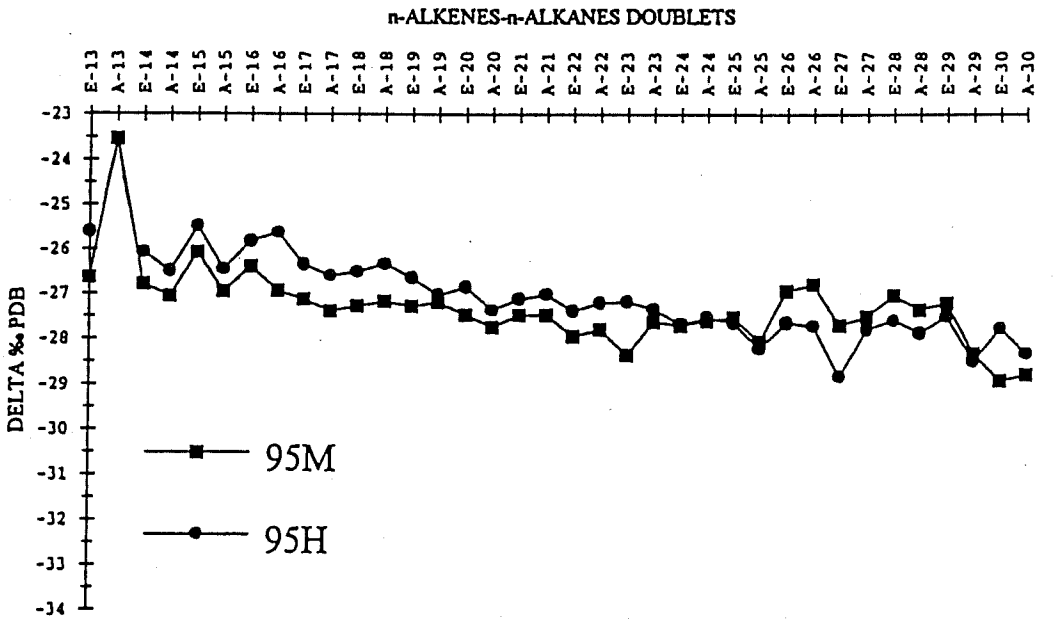
C31
C17


n-ALKENES-n-ALKANES DOUBLETS
DELTA ‰ PDB
95F
94F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DELTA ‰ PDB
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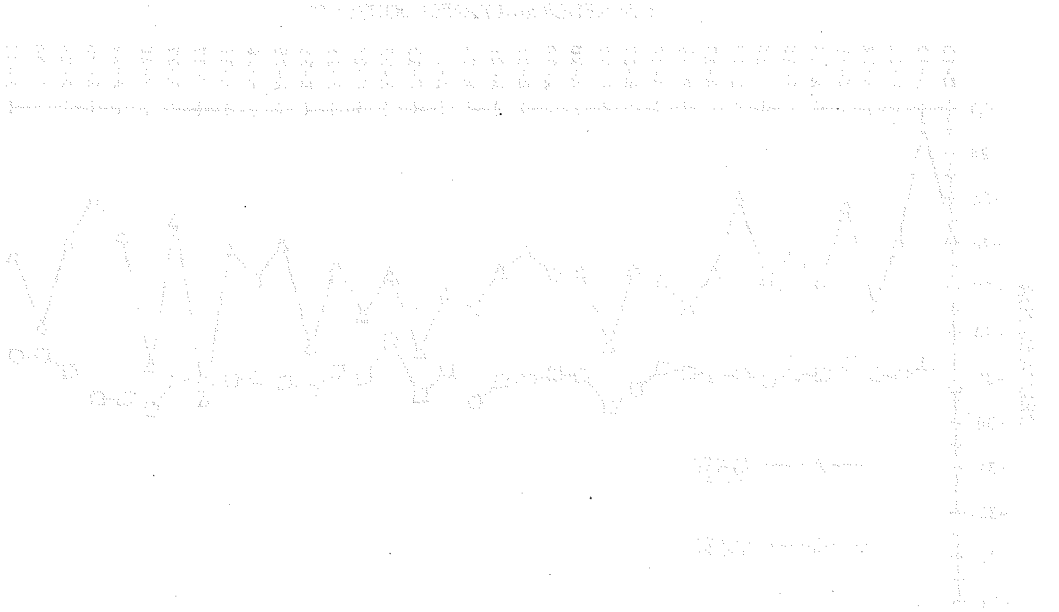
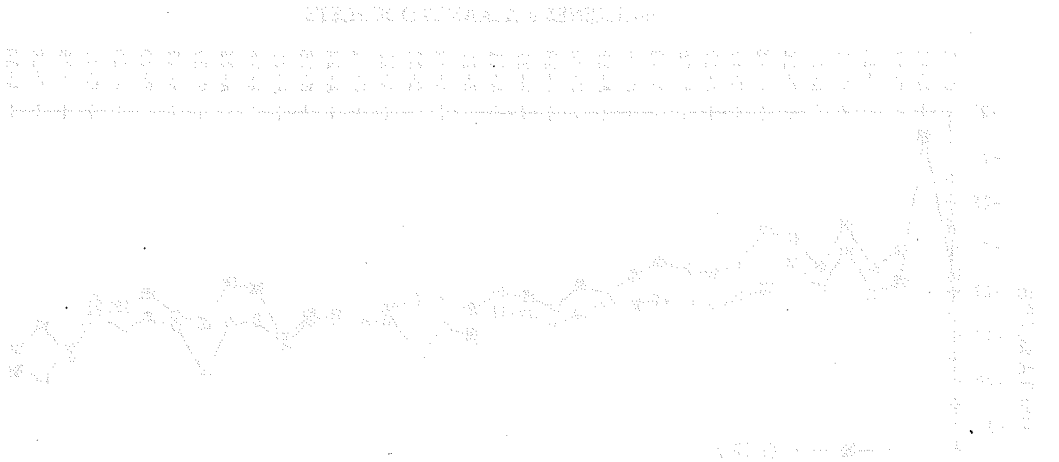
95H





Intrinsic Bioremediation of Hydrocarbons in Unsaturated Soil

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ABSTRACT

Intrinsic bioremediation of hydrocarbons in ground water is considered to be dominated by anaerobic degradation processes. Aerobic oxidation of hydrocarbons (using molecular oxygen) is limited by the abundance of oxygen in ground water, and the low rate of oxygen replenishment by molecular diffusion through water.

In contrast, intrinsic bioremediation of hydrocarbons in the unsaturated zone of soil is mainly accomplished by aerobic oxidation. In this zone, the rate of oxygen replenishment is enhanced by the high rate of oxygen transport through gaseous pore space. In addition, anaerobic oxidation of hydrocarbons in the unsaturated soil is limited by low abundance and mobility of anaerobic electron acceptors.

Biogeochemical zonations are established in contaminated soil, with the geometry of the zonation defined by the effectiveness of oxygen replenishment. As a result, most hydrocarbon biodegradation occurs within a narrow outer zone of contaminated soil, near the aerobic/anaerobic boundary. Hydrocarbon removal proceeds by continual elimination of the external layer of contamination. Estimates of the rate of hydrocarbon removal can be made by determining the rate of oxygen replenishment using molecular diffusion models and soil gas measurements.

In-situ respiration tests and soil gas analysis are used at the Unocal Guadalupe Oil Field to determine the control and rate of hydrocarbon degradation. The distribution and composition of hydrocarbons remaining in the soil are shown to be consistent with the biogeochemical zonation model and layer by layer removal of hydrocarbons. Different approaches are used to estimate the age of contamination.

INTRODUCTION

The principles governing intrinsic bioremediation of hydrocarbons in the unsaturated soil are similar to those applied to the groundwater environment. In both parts of the soil column, the biodegradation of hydrocarbons is basically an oxidative process involving the reduction of available 'electron acceptors' in the soil. The pore fluid (groundwater or soil gas), however, are different and play a major role in determining the supply of electron acceptors and, thus, the rate bioremediation. In unsaturated soil, non-volatile hydrocarbons are predominantly oxidized by *in situ* utilization of molecular oxygen supplied by soil gas. Volatile hydrocarbons (e.g. methane and benzene), on the other hand, migrate out of contaminated soil before oxidation during transit through uncontaminated soil (1).

In this paper, we will discuss intrinsic bioremediation of hydrocarbons in unsaturated soil. In the first section, the important processes active in the unsaturated zone will be reviewed. These processes include hydrocarbon degradation reactions; biogeochemical zonation and replenishment of molecular oxygen by molecular diffusive transport. Following, the data collected from a field study at the Guadalupe Oil Field, California will be discussed. For this example, soil gas data will be used to estimate the rate of hydrocarbon degradation and this rate will be compared to changes in the distribution of hydrocarbons in the soil.

HYDROCARBON DEGRADATION REACTIONS

Hydrocarbon oxidation: Aerobic conditions exist in unsaturated soil when molecular oxygen is present in the soil gas. Under aerobic conditions, the degradation of hydrocarbons usually proceeds by molecular oxygen attacking one of the terminal methyl-groups of the hydrocarbon molecule. This process transforms the hydrocarbon structure to that of the equivalent alcohol, and further degradation of the alcohol molecule occurs in the same manner as alcohol produced from other substrates besides hydrocarbons. Short and long chained fatty acids are commonly produced as intermediate steps in hydrocarbon oxidation.

Though the aerobic oxidation of hydrocarbons involves several intermediate steps, CO_2 and water are the main product of the reaction. As a result, the overall reaction can be written to show the bulk change in the amount of hydrocarbon, oxygen, CO_2 and H_2O involved in the reactions. For petroleum, the wide variety of hydrocarbons present can be divided into two major classes, aliphatics and aromatics, which differ significantly in the amount of oxygen needed for biodegradation. Typical oxidation-reduction reactions for aliphatic (hexane) and aromatic (benzene) hydrocarbons are shown below:

1a) $C_6H_{14} + 9.5\ O_2 = 6\ CO_2 + 7\ H_2O$ [hexane]

1b) $C_6H_6 + 7.5\ O_2 = 6\ CO_2 + 3\ H_2O$ [benzene]

The oxidation-reduction reaction involves electron transfer and change of valence state for certain atoms between reactants and products. For aerobic oxidation of benzene, the valence of carbon changes from -1 in benzene to +4 in CO_2. Electron balance is retained by the valence of oxygen atoms changing from 0 in molecular oxygen to -2 in CO_2. Oxidation-reduction reactions (unlike fermentation reactions in landfills) use more gaseous molecules (e.g. 9.5 moles O_2 for hexane oxidation) than are produced (6 moles CO_2). Thus, hydrocarbon oxidation processes in unsaturated soil don't create positive pressure in soil gas.

Molecular hydrogen can be produced as a byproduct of hydrocarbon biodegradation. The H_2 is a product of the electron transfer process; it is unstable under aerobic conditions; and should be readily removed from aerobic soil gas. Because of its high mobility, however, hydrogen can apparently escape from the biofilm (the active biodegradation site) and significant levels of molecular hydrogen (>1%) can develop in soil gas related to contaminated soil (1).

Anaerobic hydrocarbon oxidation: With the elimination of oxygen (anaerobic conditions), other electron acceptors in the natural environment become active for oxidation of organic matter (3). In order of preference, the significant anaerobic electron acceptors in nature include nitrate, manganese, ferric iron and sulfate. In groundwater, dissolved sulfate and nitrate are usually the most important anaerobic electron acceptors available for hydrocarbon oxidation (4). However, due to their high water solubilities, nitrate and sulfate are generally only minor components in unsaturated soils. As a result, mineral iron (5) and manganese are probably the dominant anaerobic electron acceptors present. Both are limited in mobility and, therefore, the contribution of anaerobic oxidation mechanisms to overall hydrocarbon degradation is considered small in unsaturated soil.

Methanogenesis reactions: Two separate biochemical pathways, CO_2 reduction and fermentation, are important for methane generation (methanogenesis) in a wide variety of natural anaerobic environments, including marine/lacustrine sediments, swamps, paddy soils, sewage digestors and landfills. Because of physiological limitations, methane producing bacteria are incapable of direct metabolism of large organic molecules and methanogenesis by fermentation is limited to a few small organic molecules, with acetate being the most important in the natural environment.

Though the CO_2 reduction reaction is kinetically more favorable than fermentation, other environmental factors usually control which of the methanogenesis reactions occurs in a particular environment. For aqueous environments, the stable isotope ratios (hydrogen and carbon) of methane can be used to determine the pathway of formation (6; 7). For unsaturated soils,

however, the stable isotope ratio (carbon) of CO_2 is needed to determine the pathway of formation (8).

Based on laboratory studies using ligno-aromatic compounds (9), aromatic acids (10) and aromatic hydrocarbon (11), it is now widely accepted by environmental scientists that anaerobic degradation of aromatic hydrocarbons can occur in groundwater and result in methanogenesis. This reaction, as shown below for benzene (4), doesn't involve an external anaerobic electron acceptor:

2) $$C_6H_6 + 4.5\ H_2O = 3.75\ CH_4 + 2.25\ CO_2$$

The intermediate steps and stable isotopic fractionation involved in the above reaction have not been defined. However, it is anticipated that the CO_2 and CH_4 produced from the reaction would have stable isotope ratios equivalent to those obtained from the acetate fermentation reaction.

BIOGEOCHEMICAL ZONATION

For the degradation of organic matter, the sequence of different reactions, or ecological succession (3), alters the geochemical characteristics of the environment leading to biogeochemical zonation. A general outline for these zones in unsaturated soil is given in (1) and the characteristics of these zone can be summarized as below:

- Uncontaminated soil - soil gas contains oxygen (aerobic conditions) and volatile hydrocarbons derived from the contaminated zone may be present. Volatile hydrocarbons are transported by molecular diffusion and oxidized by aerobic respiration.
- Outer rim of contaminated soil - zone of intense hydrocarbon oxidation, with oxygen being replenished from uncontaminated soil. Under certain soil conditions, the content of molecular hydrogen in the soil gas can reach significant levels, inducing molecular diffusion into adjacent zones (1). Anaerobic conditions may also exist on a micro-scale within biologically active biofilms.
- Anaerobic hydrocarbon oxidation zone - interior to the aerobic oxidation zone. This zone has not been well documented in unsaturated soil and is probably limited in size and importance. The zone is anaerobic and available electron acceptors (mainly mineral iron/manganese) will be reduced.
- Anaerobic methanogenesis zone - anaerobic electron acceptors are depleted from the soil. Methane generation occurs by one of major pathways, dependent on transport of acetate and/or hydrogen from the hydrocarbon oxidation zones. Hydrogen transport and CO_2 reduction have been shown to

the dominant processes in unsaturated soil (1). Transport and fermentation of acetate have not been well documented in unsaturated soil.

The important consequence of biogeochemical zonation in unsaturated soil is that most hydrocarbon degradation occurs only in the zone of oxygen penetration. Based on available data, methanogenesis is a sub-set of the hydrocarbon oxidation process, utilizing molecular H_2 that diffuses into the interior anaerobic environment for CO_2 reduction.

OXYGEN REPLENISHMENT IN UNSATURATED SOIL

Direct observations through continuous (sensor) and discrete (gas chromatography) soil gas measurements at numerous sites with petroleum contamination (gasoline, diesel, solvents, and crude oil) indicate that biodegradation is almost always limited by the availability of oxygen, especially with TPH contents above 3000 ppm. Therefore, the rate of hydrocarbon degradation reactions in unsaturated soil can be estimated from the rate of oxygen/CO_2 fluxes into and out of the soil. These estimates can be made using molecular diffusion equations, modified for application to unsaturated soil (12):

5) $$F = - (D * n) / t * dC/dz$$

where:

F = flux of component in units quantity/area-time
D = the bulk molecular diffusion coefficient for given component
n = gas-filled porosity
t = tortuosity = $n^{1/3}$ for dry soils and $t = n^{1/3} * [n / n + n_w]^2$ for wet soils
where n_w = moisture content (13)
dC/dz = concentration gradient in soil gas

Oxygen and CO_2 concentration gradients can be determined by collecting soil gas samples at different depths in the unsaturated zone. In order to calculate total flux of electron acceptors and to estimate overall degradation rate for a subsurface hydrocarbon plume, it is best to measure the soil gas gradients in the zone where the in-situ respiration rate is near zero. This biogenically inactive zone is normally found in uncontaminated soil above the plume and below the rhizosphere, if present. For most soil types, valid soil gas data can generally be obtained. For dry soil with gas-filled porosity greater than 15 %, the data usually yields linear or sub-linear concentration gradients with depth. For typical soil conditions and the contamination (anaerobic conditions) at 10 feet, it will take about 1 year to oxidize a 3 foot thick layer of contaminated soil with 1000 ppm TPH.

GUADALUPE OIL FIELD: A CASE STUDY

Guadalupe Oil Field is located in coastal central California. At the site chosen for study, the soil consisted of beach sand and the groundwater table is at about 14 feet. Petroleum product exists on the ground water and, due to rise and fall of the water table, has coated sand grains across the depth interval from about 11 to 20 feet. Most of the product has been subsequently removed by pumping in recent years.

Four sample sites were place linearly at 10 foot intervals over the central part of the plume. At the two end sites, soil gas data were collected at 2 foot intervals from the surface to the groundwater table using hand auger and soil gas probes. Samples were analyzed for O_2, CO_2 and methane contents by using laboratory and field instruments. At all four sites, cores were taken from the depth intervals from 8 to 19 feet depth in 1-inch or 2-inch clear plastic liners, using a Geoprobe. The cores were sampled at 2 foot intervals and soil samples were solvent extracted and analyzed for molecular composition by FID gas chromatography (GC).

For continuous soil gas measurements, subsurface carbon dioxide and oxygen sensors were installed near the sample locations at depths of 7 feet and 11 feet. An air injection point with a 2-foot screened interval was also installed at 11 feet depth for in-situ respiration measurements (14).

Results: Hydrocarbon profiles in soil and soil gas are shown in a plot of methane and hydrocarbon extract contents versus depth, using data for all locations (Figure 1). In the top 8 feet of sand, the methane content is less than 20 ppm. Below 8 feet, the methane content increases 1-2 orders of magnitude within a 2 foot interval. Similarly, the hydrocarbon content in the top 8 feet of sand is less than 100 ppm. It increases to over 10,000 ppm at depths between 9 - 13 feet. The mean content for 11 samples taken at or below 13 feet is 37,000 ppm.

Soil gas profiles of O_2 and CO_2 versus depth (Figure 2) are based on discrete soil gas samples taken at the two sample locations mentioned above. Continuous oxygen measurements made over a 2-week period (sensor analysis every minute) fall between 11% and 12% for two oxygen sensors placed at 7-foot depth and between 1% and 4% for four oxygen sensors placed at 11-foot depth. The concentration gradients for both O_2 and CO_2 are fairly linear in the top 8 feet of sand. The gradients are estimated to be 1.2 mole-%/ft. and 1.0 mole-%/ft., respectively.

The petroleum product on the water table consists of hydrocarbons in the diesel range, where the normal alkane and isoprenoid molecular distribution is consistent with the unweathered diesel (15). None of the soil samples taken at 9 feet have any indication of diesel-ranged hydrocarbons present. All samples taken

at 11 feet have a distinctive 'hump' in the diesel range. The only other feature for these samples is the internal standard (IS) that elutes just before nC20. The GC traces for samples taken below 13 feet have the suite of n-alkanes extending from C10 to C28 and the suite of isoprenoids between nC12 and nC19. The GC traces for samples taken at 11, 13 and 17 feet are shown in Figure 3. Hydrocarbons in soil samples taken between 13 ft. and 15 ft. have very similar GC patterns and, on the basis of n-alkane/isoprenoid ratios, are distinctively different from those taken below 15 feet. For example, the nC17/Pr ratio for samples below 15 feet ranges from 2.1 to 2.5 and the ratio for samples between 13 and 15 feet ranges from 1.2 and 1.6.

Rate of hydrocarbon degradation: Our in-situ respiration tests were made to determine the potential rate of aerobic degradation in the soil if molecular oxygen was not limited to the system. At 7-foot depth, consistent with the lack of hydrocarbons, no measurable respiration rate was found at the two oxygen sensor locations. In contrast, very high respiration rates (near 10% O_2/day) were determined from all oxygen and carbon dioxide sensor data (14) from 11-foot depth. The 11-foot respiration rate corresponds to a hydrocarbon degradation rate of 10 mg/L/day, assuming a soil porosity of 0.25 for the site. For this degradation rate, the 37,000 ppm hydrocarbons in the soil will be removed in approximately 5 years.

On the basis of the biogeochemical zonation model, oxygen is absent from most of the hydrocarbon contaminated soil. Consequently, hydrocarbon degradation is only significantly near the aerobic/anaerobic transition zone, where the rate of biodegradation is limited by the amount of transport (or flux) of oxygen from the overlying soil. The aerobic-anaerobic transition is near 11 foot depth, and there is no evidence of residual hydrocarbons above 9 foot depth (Figure 1). Therefore, the active biodegradation zone is probably within a 1-2 foot soil layer defined by the coexistence and reaction of electron doners (hydrocarbons) and electron acceptors (oxygen). The lack of significant degradation below this layer is consistent with the relatively unweathered hydrocarbon composition in soil samples at and below 13 feet (Figure 3).

The molecular diffusion equation (5) was used to determine the flux of O_2 and CO_2 in and out of the soil. Based on a porosity of 0.25 and concentration gradients of 1.2 mole-%/ft. for O_2 and 1.0 mole-%/ft. for CO_2, the fluxes for O_2 and CO_2 are estimated to be 0.42 and 0.26 moles/m^2-day, respectively. Assuming initial soil hydrocarbon content of 37,000 ppm, it would take roughly 15 years to completely degrade a 1-foot layer of hydrocarbons, using the oxygen flux determined above and an oxygen utilization factor of 3.5 for aliphatic hydrocarbons. The actual oxygen flux can be seasonally lowered by high moisture content in the sand.

Estimated age of contaminated soil: Based on the coloration of sand observed during soil sampling and the lack of diesel-ranged hydrocarbons, it is assumed that the 9 foot depth is above the top of the historical contaminant level. The diesel humps present in all other GC traces indicate that the top of the contaminated soil is currently near or just above the 11 foot depth. Though a significant amount of hydrocarbons (an average of 2,300 ppm) remain at 11 feet, over 90% would have been removed if the initial concentration was similar to the deeper samples (mean 37,000 ppm). In contrast, the amount of hydrocarbons in the 13 foot samples is not significantly lower than the deeper samples. Therefore, the highly active biodegradation zone is considered to have advanced 2 feet (above 11 to above 13 feet) or less with time. This advancement would correspond to a maximum age of 30 years for the contamination to be biodegraded.

The nC17/Pr ratio has been used to estimate the age of diesel spills at various locations in Europe (15). In the European study, the nC17/Pr ratio of unweathered diesel is considered to be 2.3, which is within the range (2.1 to 2.5) for samples between 17-19 feet from this study. Age determination for the diesel spills are based on a calibration curved developed for nC17/Pr ratios of samples collected at 2 feet depth within the spill margin. For this study, samples from 2 feet within the contaminated zone (13 - 15 feet) have nC17/Pr ratios (1.2 to 1.6) that correspond to a weathering age between 6 and 9 years, using the calibration curve from (15).

CONCLUSION

In situ respiration tests, along with discrete (GC analysis) and continuous (sensors) soil gas analyses, were used to evaluate the control and rate of intrinsic bioremediation of petroleum hydrocarbons from contaminated soil at the Unocal Guadalupe Oil Field. The results from this study are evaluated using the biogeochemical zonation model for degradation, and yield an estimated removal of a hydrocarbon layer (37,000 ppm) 2 feet or less in thickness during the last 30 years (or less) residence time in the soil.

The molecular composition of hydrocarbons were determined for samples collected perpendicular to the trend of the contaminated soil layer. Consistent with the biogeochemical zonation model, there is no evidence of biogenic alteration for samples below 4 feet from the top of the contamination zone. Samples between 2 and 4 feet from the top of the contamination zone show evidence for slight alteration by biodegradation, with the nC17/Pr ratios indicating an age estimated between 6 and 9 years, according to the calibration curve from (15). Samples within the top 2 feet of the contamination zone are extensive biodegradation, with loss of over 90% of the petroleum hydrocarbons.

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Figure 1. Depth distribution of methane (mole-% soil gas) and extract (ppm) at Guadalupe Field beach site. Present-day water table is at about 14 feet.

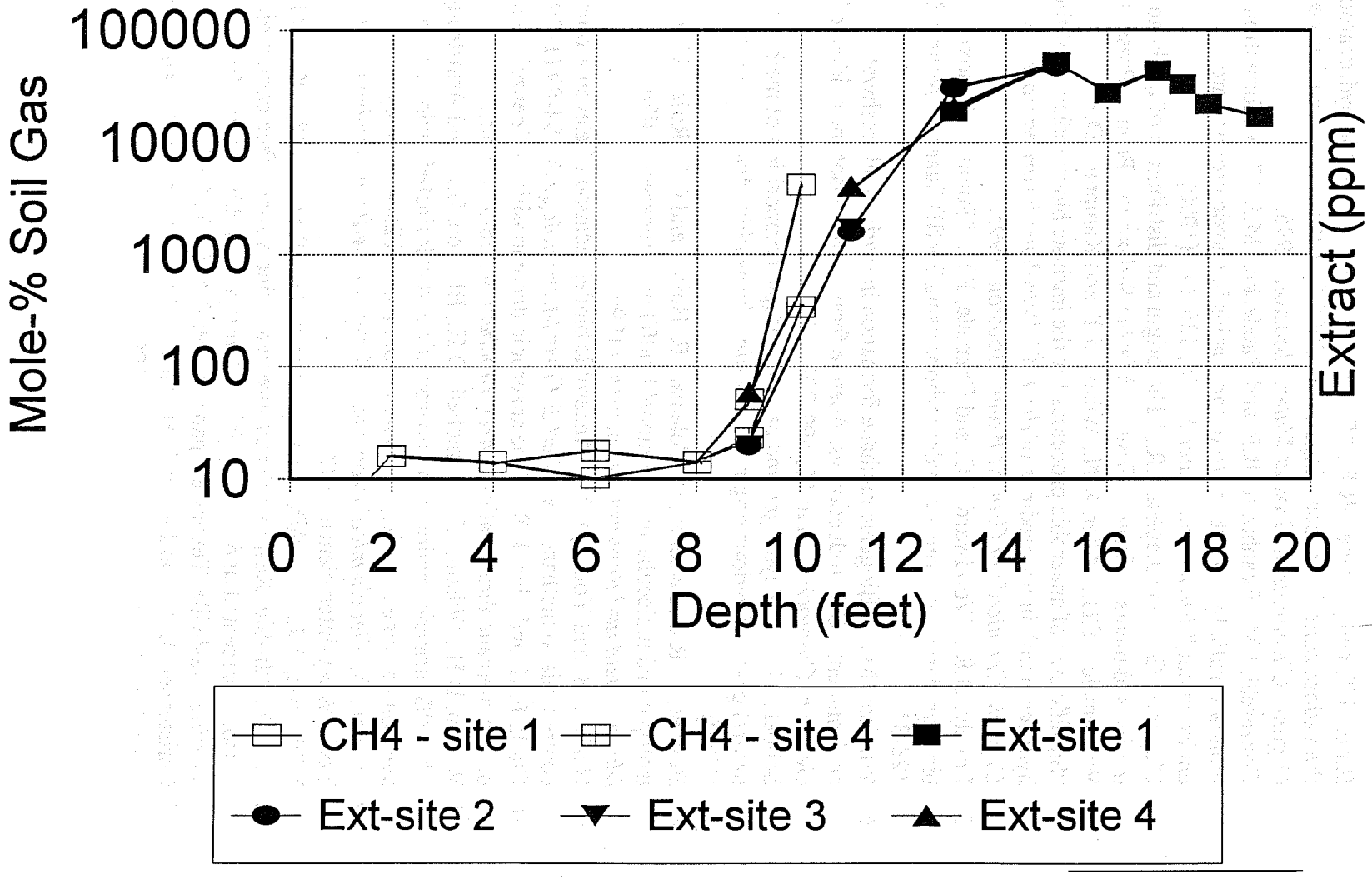
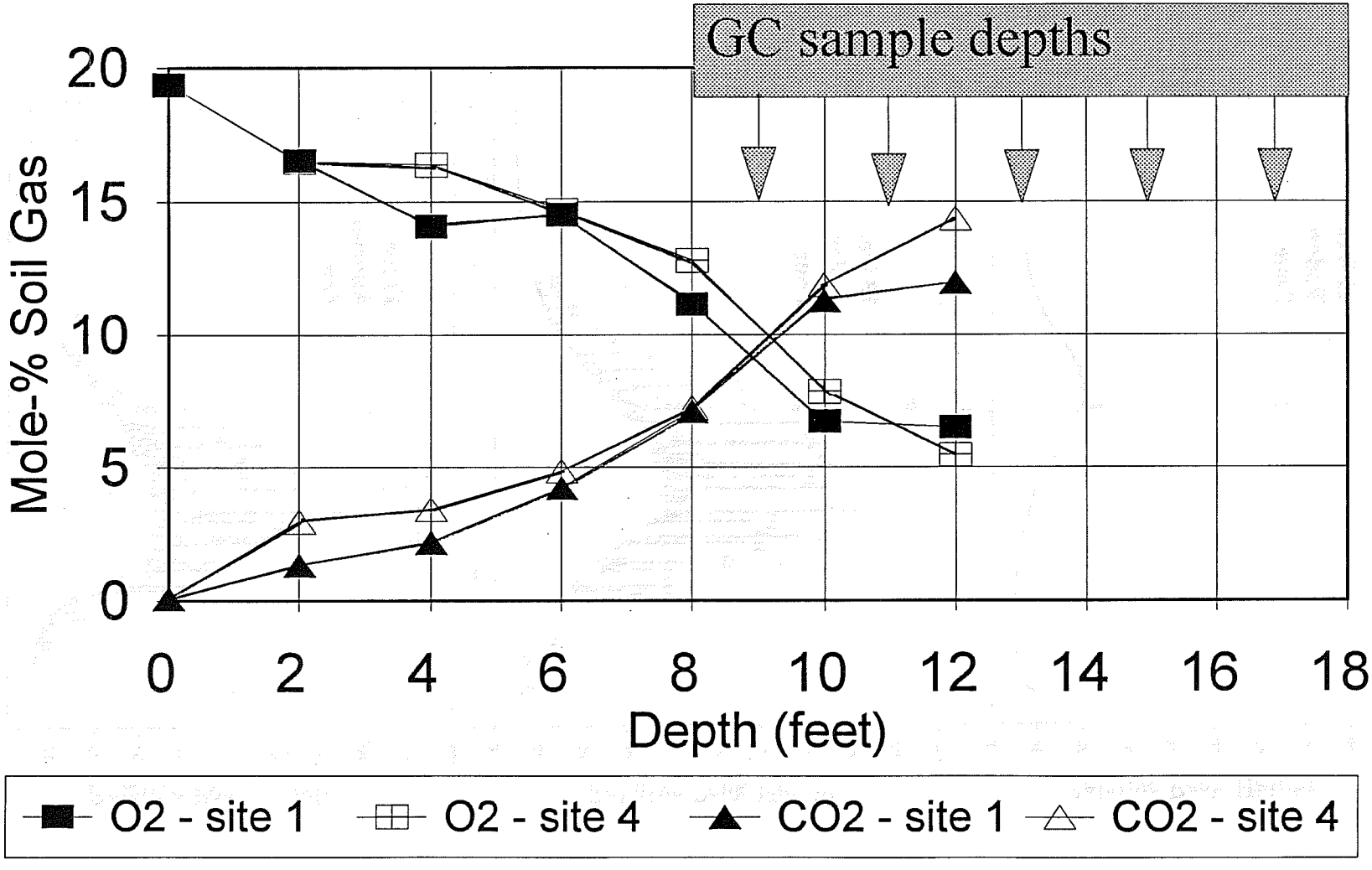


Figure 2. Depth distribution of oxygen (mole-% soil gas) and carbon dioxide (mole-% soil gas) at Guadalupe Field beach site. Depths are indicated for GC analysis of extracts.



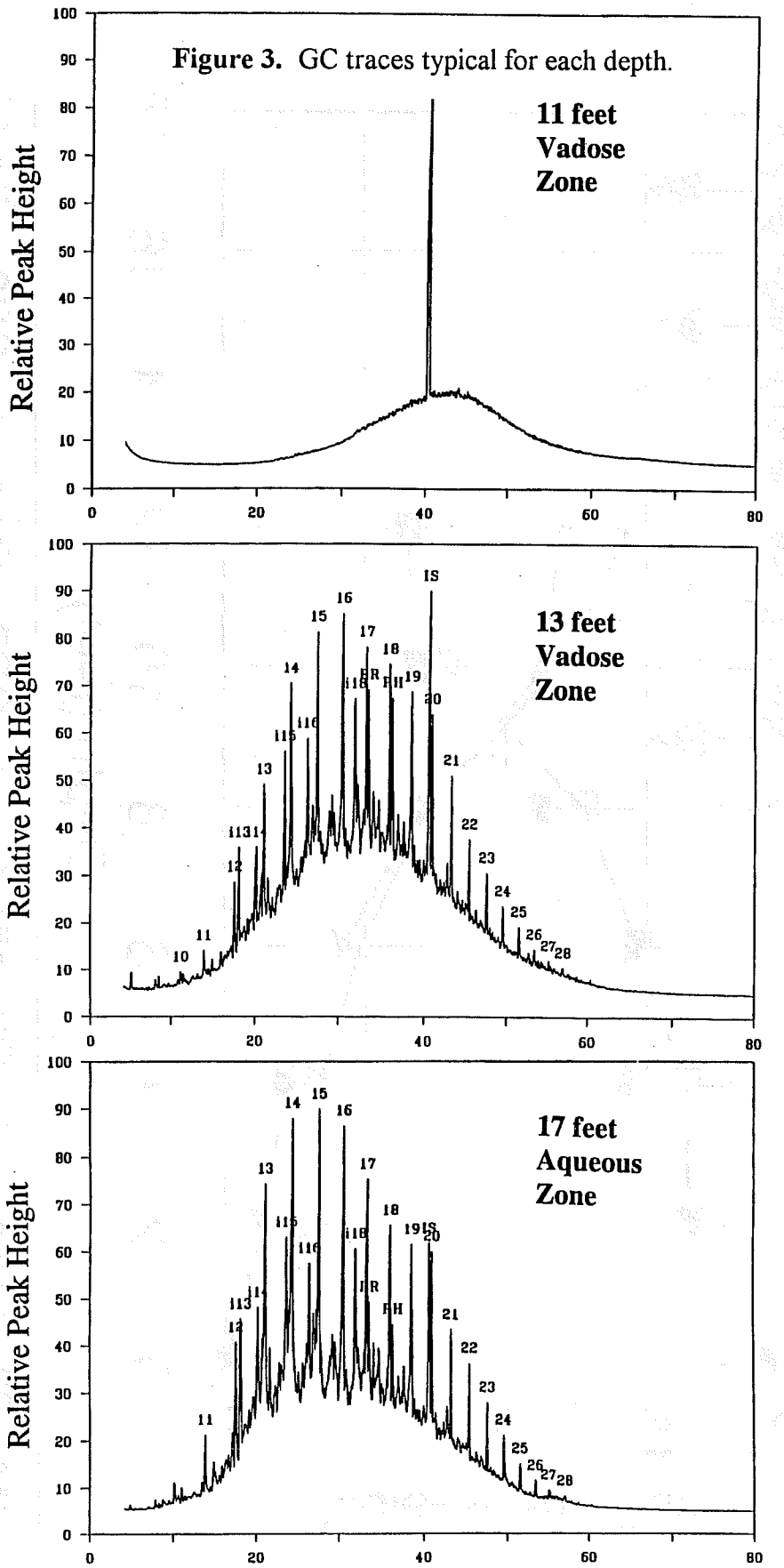


Figure 3. GC traces typical for each depth.
Relative Peak Height
11 feet
Vadose
Zone
13 feet
Vadose
Zone
17 feet
Aqueous
Zone

Plant and Microbial Influence on Bioremediation of Hydrocarbon-Contaminated Soils

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ABSTRACT

The rhizosphere soil adjacent to the plant root exhibits high microbial activity that may enhance hydrocarbon contaminant biodegradation. We amended a soil with an organic contaminant mixture (OCM) containing equimolar amounts of benzoic acid, hexadecane, 2,2-dimethyl 4,n-propyl-benzene, phenanthrene, pyrene, and *cis*-decahydronaphthalene or cycloheptane to evaluate plant species that can satisfactorily grow in contaminated soils and enhance the potential for microbial decomposition of contaminants in the rhizosphere. In a plant screening of four legumes, four grasses, and one composite exposed to 0, 1000, 2000, 4000, or 8000 mg OCM/kg, plant growth was reduced at the 4000 and 8000 mg/kg rates. At 1000 and 2000 mg OCM/kg, root length and root dry weight of alpine bluegrass (*Poa alpina* L.) increased. Root growth for the remaining plant species generally decreased as OCM rate increased.

In a subsequent study, alpine bluegrass and alfalfa (*Medicago sativa* L.) were grown in soil amended with 0 or 2000 mg OCM/kg. After 14 weeks of growth in contaminated soil, root dry weight of alfalfa and alpine bluegrass decreased 97% and increased 235%, respectively, compared to the controls. None of the components of the OCM were found in shoot or root tissue. At 9 weeks, the organic contaminant degrader (OCD) population was significantly greater in rhizosphere and contaminated soils than in bulk soil and non-contaminated soil, respectively. Alfalfa and bluegrass rhizosphere OCD populations were tenfold greater in the contaminated than in the non-contaminated soils. Selective enrichment of OCD populations was observed in contaminated rhizosphere soil.

Root growth in contaminated soil is also influenced by contaminant location and characteristics. We grew cold tolerant plant species, Arctared fescue (*Festuca rubra*, L.) and tall fescue (*Festuca arundinacea* Schreb.), in columns containing alternating layers of soil with either 0 or approximately 20000 mg/kg total petroleum hydrocarbons (TPH) of weathered bunker C fuel oil or approximately 3500 mg/kg TPH of diesel.

Contamination with bunker C at the 15 to 30 cm soil depth stimulated root growth throughout the soil column compared to the non-contaminated treatment. Diesel, a more volatile contaminant, had a more deleterious impact on plant growth.

Our studies demonstrated that plants can germinate and grow in contaminated soil, that relative to the bulk soil there is an increase in the percentage of the rhizosphere microbial population capable of degrading contaminants, and that roots of select plants can explore contaminated soil. These data support the hypothesis that bioremediation of petroleum contaminated-soil can be enhanced by growth of appropriate plant species.

INTRODUCTION

Soils contaminated with organic chemicals represent a serious environmental problem. Stimulation of contaminant decomposition by enhancing rhizosphere-microbial activity would provide a low-cost, relatively non-invasive, and environmentally sound solution. Treating large-scale, near-surface contaminated zones in the soil would also lessen the potential for ground or surface water pollution. Success of rhizosphere enhanced remediation depends upon the ability of plant roots to stimulate the growth and activity of soil microbial populations that can decompose organic contaminants. We hypothesized that plant characteristics, including root length, root growth rate, root density, soil volume influenced by roots, and changes in rhizosphere microbiology would be important precursors to rhizosphere-enhanced remediation.

Processes contributing to rhizosphere enhanced remediation are generally understood, however, information on development of management strategies, including appropriate plant species for different contaminants and environmental conditions, is limited. We have conducted plant screenings and soil incubations to identify plant species that can germinate and grow in contaminated soils and stimulate microbiological activity in the rhizosphere.

Low mass-transfer rates of contaminants in soil also limit in-situ bioremediation. As a result of the heterogeneous distribution of carbon, moisture, and nutrients which are essential for microbial activity, remediation occurs unevenly in soil. Roots actively explore soil during growth and increase the amount of rhizosphere soil. This process may provide a low-cost means to reduce mass-transport limitations. There is currently little information on root distribution in contaminated soils.

Our objectives were to: i.) determine if plants can germinate and grow in contaminated soils, ii.) evaluate the potential for enhanced degradation ability in rhizosphere soils relative to bulk soils, and iii.) determine if contaminated soil zones alter root growth and distribution.

MATERIALS AND METHODS

Plant Screening

In our initial plant and microbial characterization studies, we amended soil with an organic contaminant mixture (OCM) that contained an equimolar mixture of benzoic acid, hexadecane, 2,2-dimethyl 4,n-propyl-benzene, phenanthrene, pyrene, and *cis*-decahydronaphthalene or cycloheptane. Four legumes: red clover (*Trifolium pratense* L.), alfalfa (*Medicago sativa* L.), white clover (*T. repens* L.), and birdsfoot trefoil (*Lotus corniculatus* L.); four grasses: alpine bluegrass (*Poa alpina* L.), Bering hairgrass (*Deschampsia beringensis* Hulten), reed canarygrass (*Phalaris arundinacea* L.), and quackgrass (*Elytrigia repens* Nevski); and one composite, tilesy sage (*Artemisia tilesii* Ledeb.), were evaluated for their ability to grow in contaminated soil. Plants were grown in replicate for 6 wk at 25°C and 10 wk at 10°C on a Captina silt loam soil (fine-silty, siliceous, mesic Typic Fragiudults) amended with the OCM at rates of 0, 1000, 2000, 4000, or 8000 mg/kg. After harvest, root lengths were calculated and root and shoot dry weights were measured. Root and shoot tissue and soil subsamples from each flat were analyzed for presence of the OCM compounds using gas chromatography analysis. Additional details are given by Rogers et al. (1).

Rhizosphere Microbial Populations

Alfalfa and alpine bluegrass were grown in a fine sandy loam or Captina silt loam. The soils were placed in 2.0-L jars, pre-incubated five wk at 25°C, and amended with 0 or 2000 mg OCM/kg before planting. Treatments were replicated three times and compared to uncontaminated controls, with and without plants. Soils and plants were destructively sampled 0, 4, 9, and 14 wk after planting. Because of differences in germination rates, the first measurements occurred after 9 wk for bluegrass and after 4 wk for alfalfa. At harvest, rhizosphere soil (soil adhering to roots) and non-rhizosphere soil was collected from each jar and serially diluted. Total organic contaminant degrader (OCD) populations, or microorganisms capable of using one or more of the OCM compounds as a sole carbon source, were enumerated using the Most-Probable-Number (MPN) technique. The MPN tubes contained Bushnell-Haas medium amended with resazurin as a redox indicator. The dilution plate technique was used to determine total bacterial and fungal numbers using tryptic soy agar and Martin's Medium, respectively. Harvested plant tissue and soil samples were analyzed for the OCM compounds. Additional details are given by Nichols et al. (2).

Root Distribution

We used columns, that measured 10.2 cm ID by 90 cm long, to observe the effects of contaminated soil layers on root growth and distribution (3). Columns were filled and uniformly packed with soil to a bulk density of approximately 1.3 g/cm^3. Two contaminated soils were

used. One soil was obtained from Dutch Harbor, Alaska, had an organic matter content that ranged between 5.6 and 10.2%, and was contaminated with a heavy, weathered petroleum fraction, believed to be from post WWII ruptured bunker C fuel-oil tanks. Concentrations of bunker C constituents in the soil varied between 16000 to 25000 mg/kg total petroleum hydrocarbons (TPH) and 4000 to 5000 mg/kg diesel range organics (DRO). We prepared a diesel-contaminated soil by adding diesel to soil, frequently mixing, and aging in a laboratory fume hood for 7 days. Contaminant concentrations in the soil amended with diesel were 3000 to 4000 mg TPH/kg and 600 to 1000 mg DRO/kg. In the columns, a single thickness of approximately 15 cm of the contaminated soil layer was placed below a 15 cm layer of non-contaminated soil and also was underlain by non-contaminated soil. Either tall fescue or Arctared fescue, both cold-tolerant and readily available plant species, were seeded. Plants were thinned to one plant per column to allow for root-soil separation at harvest. At each sample time, roots and soil were removed from the columns. Soil and the associated roots in each zone were kept separate from other zones. Soil and roots were initially separated manually, followed by washing the roots over a screen to remove soil adhering to the roots. Plant tissue was stored at 4°C prior to analysis. Shoot and root dry weights were determined by drying plant material to constant weight at 65°C. Root lengths and surface areas were determined from the line intersect method.

RESULTS AND DISCUSSION

Plant Screening

Germination rates were generally greater than 50% for seeds planted in soil contaminated with 0, 1000, and 2000 mg OCM/kg (data not shown). The OCM rates $\geq$4000 mg/kg at both 10 and 25°C resulted in germination rates of <50% for several plant species. No plants germinated at 8000 mg OCM/kg at 25°C, although all plants germinated at this OCM concentration at 10°C. Contaminant effects on shoot and root growth differed among plant species and incubation temperatures. Shoot dry weight of alpine bluegrass grown at 10°C increased more than 185% in response to 1000 and 2000 mg OCM/kg compared to alpine bluegrass grown in uncontaminated soil (Fig. 1). Bering hairgrass, tilesy sage, and white clover exhibited increased shoot dry weight at 10°C at 1000 mg OCM/kg compared with the uncontaminated controls, although 2000 mg OCM/kg inhibited growth. Similar responses were observed with root lengths for Bering hairgrass and white clover. Growth of all plant species was either inhibited or reduced at 4000 and 8000 mg OCM/kg at both temperatures and growth was considered unsatisfactory for adequate plant establishment. None of the OCM compounds were detected in plant tissue at harvest.

The screening study demonstrated that selected plants could germinate and grow in soil uniformly contaminated with OCM. Because plants have increased susceptibility to stress at seedling stage, 2000 mg OCM/kg is a conservative concentration for the upper range of soil OCM concentrations that did not significantly inhibit plant growth. The enhanced growth of alpine bluegrass in the OCM contaminated soil has been replicated in additional studies (1). Stimulated root and shoot growth in response to low levels of contaminant suggested that these plants may develop vigorous root systems in contaminated sites and provide greater opportunity to stimulate rhizosphere organisms and subsequent contaminant decomposition.

Rhizosphere Microbial Populations

Based upon the results of the plant screening study, alpine bluegrass and alfalfa were grown for 14 wk in soil contaminated with 0 or 2000 mg OCM/kg. After 14 wk, shoot and root dry weights and root length of alfalfa were 97% lower in OCM-contaminated soil. In contrast, shoot dry weight, root dry weight, and root length of alpine bluegrass after 14 wk were 135, 235, and 268% greater in OCM-contaminated soil. The stimulated growth of the alpine bluegrass in response to the OCM was consistent with measurements in the plant screening study. No OCM compounds were detected in plant tissue. Except for pyrene, less than 5% of each of the compounds in the OCM were recovered from the soil 14 wk after planting (1).

In soil without plants, the addition of 2000 mg OCM/kg significantly increased the bacterial population compared to the 0 mg OCM/kg rate (2). Fungal levels showed a decrease in the contaminated soil at 9 wk that was most likely due to competition from the larger bacterial population. Bacterial and fungal populations in the rhizosphere of the alfalfa plant were significantly larger than in the bulk or non-rhizosphere soil at 9 wk.

After 9 wk, the OCD populations were significantly greater in soil amended with 2000 mg OCM/kg than the control when no plant was present (Fig. 2). When alfalfa or bluegrass was grown, the OCD levels were also significantly higher at the 2000 mg OCM/kg than at the 0 level (Fig. 2). The OCD levels were significantly higher in the rhizosphere soil compared to the non-rhizosphere or bulk soil (Fig. 2). These data show that the addition of the OCM increased the microbial population capable of degrading the added organic compounds and that the presence of the plant root stimulated the development of the degrader population. In an allied study, we have shown increased OCM degradation in rhizosphere treatments (C.S. Pidgeon, 1996, personal communication).

Root Distribution

The contaminant type influenced shoot and root growth. Diesel inhibited plant growth at lower TPH levels than the weathered bunker C (3). Although weathered by mixing and aerating in a laboratory hood, diesel retained a relatively greater percentage of petroleum contaminants as DRO compounds than the weathered bunker C. The DRO compounds have smaller molecular weights and greater water solubilities than those in bunker C; thus, they are more mobile and more prone to biological uptake.

Tall fescue root surface area was stimulated by a bunker C contaminated soil layer (Fig. 3). Enhanced growth was likely caused by a different mechanism than in the plant screening study, which used a uniformly distributed OCM. The mechanism in the columns appeared to be related to water-content differences between the control and bunker C soil treatments. The bunker C contaminated soil was hydrophobic and served to retain water in the upper layers of soil following irrigation. Increased water content could enhance root growth. Because organic contaminants are generally not uniformly distributed at field sites, there are implications for interactions between soil contaminant levels and types and soil water that should be considered in field remediation efforts.

SUMMARY

Conditions required for rhizosphere-enhanced bioremediation to occur include plant establishment, stimulation of appropriate microbial populations, and root growth into contaminated soils. These studies have demonstrated that all three can be met for petroleum compounds. Satisfactory germination and growth of plant species studied occurred in soils containing an OCM level of 2000 mg/kg. Alpine bluegrass growth was stimulated at the 1000 and 2000 mg/kg rate. The OCD population in the contaminated rhizosphere was greater than in the non-contaminated bulk soil. In rhizotron columns, we observed that roots of both Arctared fescue and tall fescue could grow into highly contaminated zones.

These data demonstrate that root growth, and hence rhizosphere effects, can occur in soils that are heavily contaminated with recalcitrant compounds present in fuels. Because these compounds are less mobile, they remain near the soil surface and are accessible to plant roots. Because rhizosphere soils can have an enhanced population of contaminant degraders, these data provide additional evidence of the potential of using rhizosphere-enhanced remediation as an option for treating hydrocarbon-contaminated soils.

ACKNOWLEDGMENTS

This research was partially supported by the Strategic Environmental Research and Development Program (SERDP), project #712, "Enhancing Bioremediation Processes in Cold Regions," and the Army Environmental Quality Technology (EQT) program, work unit AF25-RT-005 "Low Temperature Biotreatment." We acknowledge Dr. I. K. Iskandar, Chief, Geochemical Sciences Division at CRREL for his support. L. B. Perry, C.S. Pidgeon, R. N. Bailey, J. P. Lariviere, and T. J. Cary provided laboratory expertise.

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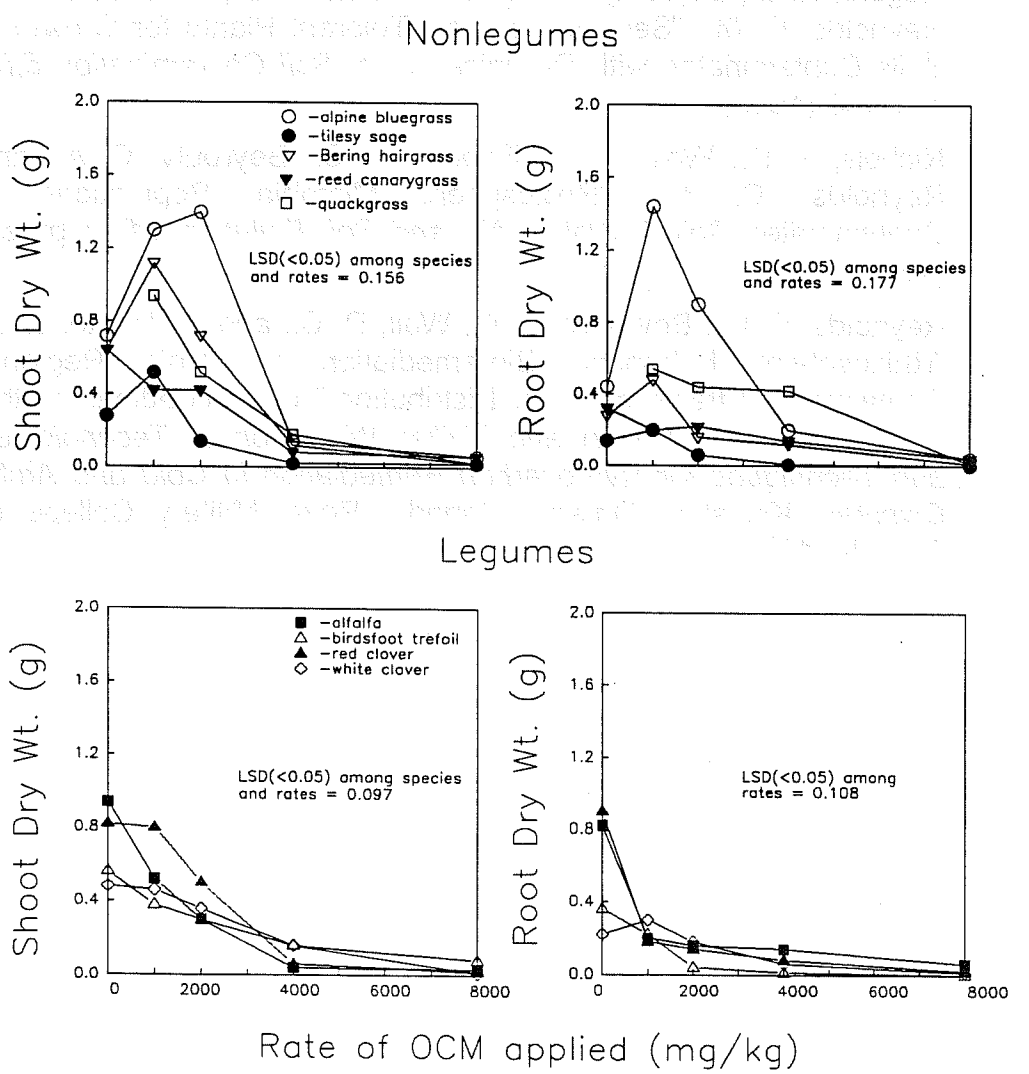

Fig. 1. Shoot and root dry weight responses of nonlegumes and legumes to an organic contaminant mixture (OCM) applied at 0, 1000, 2000, 4000, and 8000 mg/kg. Plants were grown for 10 weeks in a growth chamber at 10°C.

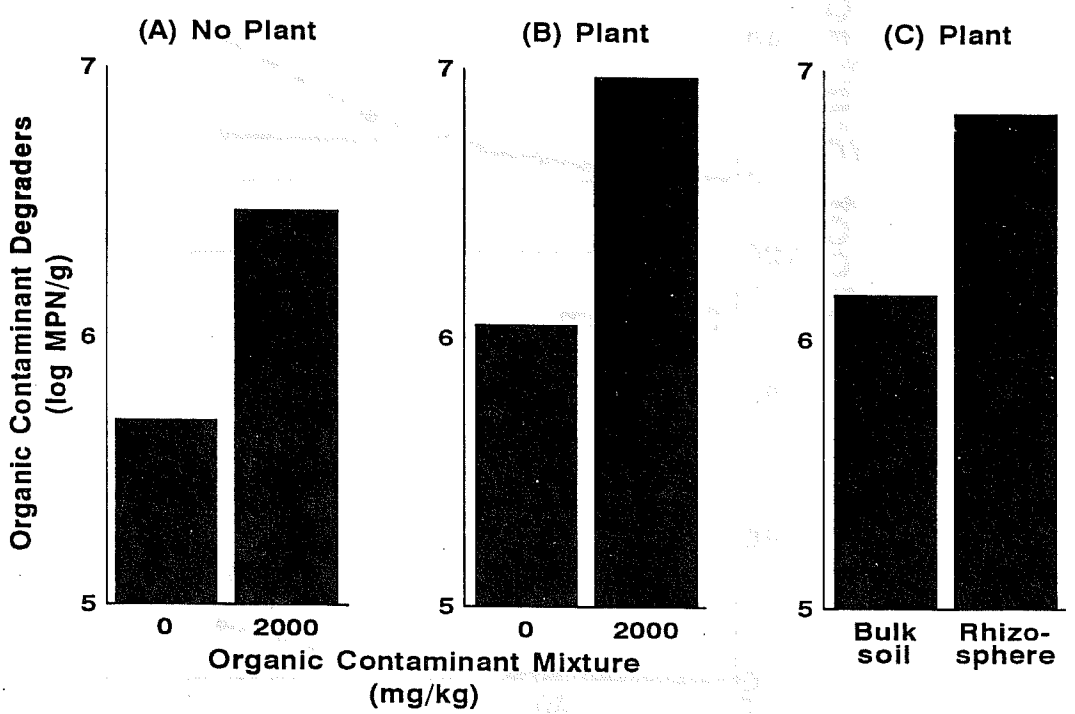

Fig. 2. Organic contaminant degrader (OCD) microbial populations after a 9-wk incubation of Captina silt loam amended with 0 or 2000 mg OCM/kg. (A) Soil without plants, (B) Soil with alfalfa or bluegrass, and (C) Bulk or non-rhizosphere soil and rhizosphere soil.

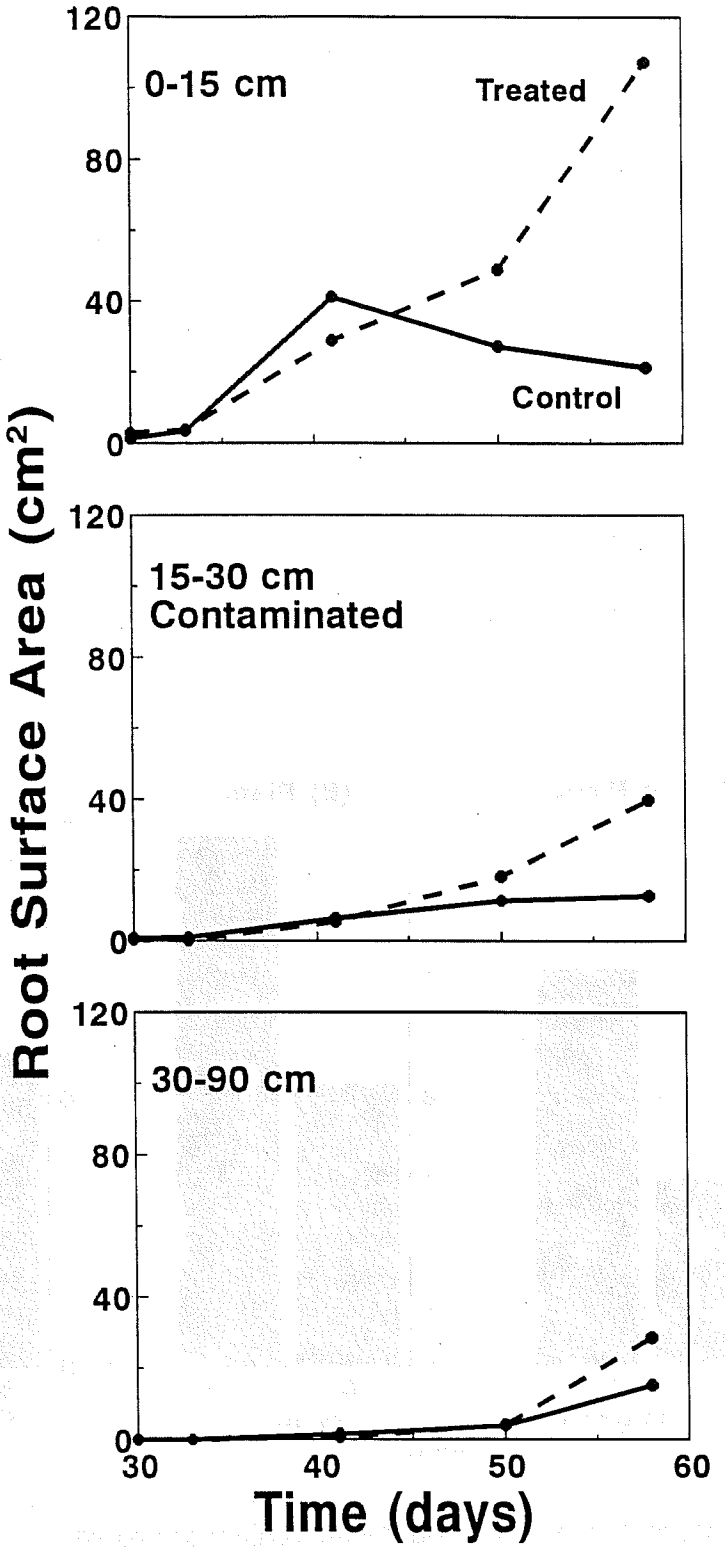

Fig. 3. Response of root surface area of tall fescue to bunker C contamination in the 15 to 30 cm depth of the Dutch Harbor soil packed in columns. Treated = tall fescue grown in the presence of the bunker C contaminated layer. Control = tall fescue grown without a bunker C contaminated layer.

Biodegradability of Gelled

Diesel-Fuel in Soils

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The general objective of this research was to study the degradation of an organic pollutant (diesel fuel) that had been solidified by a hydrocarbon gelling agent (Enviro-Tech 410). More specifically, the objective was to determine if, and to what extent, a gelled hydrocarbon (gelled diesel-fuel) was biodegradable when exposed to indigenous microbial populations present in two common southern New Mexico soils. Other objectives included the investigation of soil parameters and environmental factors that tended to promote biological breakdown.

Bench-scale biodegradation studies were conducted. Degradation was estimated by quantifying the amount of carbon dioxide (CO_2) produced. One of the soil parameters and test conditions studied was soil moisture. The results of the degradation studies indicated that, for the microorganisms indigenous to agricultural and desert soils, both diesel fuel and gelled diesel-fuel are biodegradable.

The biodegradation rate was two times higher in agricultural soils than in desert soils. However, for both soils, diesel fuel and gelled diesel-fuel biodegradation was shown to increase with an increase in the soil-moisture. The optimal soil-moisture content for biodegradation appears to be between 60 and 90 percent of field capacity.

The biodegradation results suggests that gelled diesel-fuel is a good candidate for a land application system such as landfarming which incorporates contaminants into the soil matrix and relies on microorganisms to breakdown or mineralize the wastes. The study also encourages the further assessment and identification of other important soil parameters which would be beneficial to the successful operation of a landfarming facility.

INTRODUCTION

Hydrocarbon-Specific Gelling Agents

Polymer gelling agents can be used for the chemical fixation/stabilization (CFS) of liquid pollutants such as petroleum product wastes. When petroleum products, such as diesel fuel, come in contact with the gelling agents, the diesel fuel becomes "solubilized" within the structure of the polymer [1]. The overall goal of this process is to alter the physical properties of the liquid waste. In order to maximize the effectiveness of the gelling or solidification process, chemical polymer manufacturing companies have developed polymers that are intended to target specific substances. Through "living" polymerization techniques, specialized polymer chains and architectures have been designed from a selected group of monomers, such as styrenes and butadienes [2]. The applications of these polymer gelling agents exist in the management and remediation of sites contaminated with materials such as diesel fuel and other liquid hydrocarbons.

Enviro-Tech 410

In previous research at New Mexico State University, seven different powdered and granular form hydrocarbon-specific gelling agents were studied. One of these polymers, Enviro-Tech 410 (marketed by Petroleum Environmental Technologies Inc., in Williamsburg, Michigan) proved successful in the gelling or solidification of diesel fuel [3]. Consequently, Enviro-Tech 410 was used in this research. Although the exact chemical formula and structure of the polymer is proprietary and therefore unknown it is identified in the product literature as a styrene-butadiene block copolymer. This type of architecture is an adaptation of the basic "AB block-polymer" structure, which is shown in Figure 1. Figure 2 illustrates the chemical structures of both the styrene and butadiene monomers in the block copolymer.

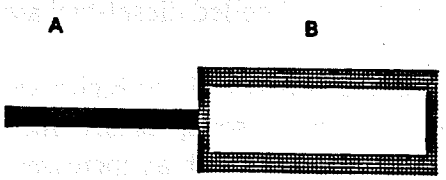

Figure 1. Basic "AB Block Copolymer" Architecture [2], [3].

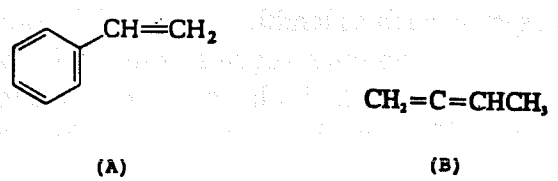

Figure 2. Chemical Structures of (A) Styrene and (B) Butadiene Monomers [4].

METHODS

Background Information

The respiration of soils can be measured in the field and in the laboratory. Measurement of soil respiration after mixing the sample with organic compounds has traditionally been used to determine if the compounds are biodegradable as well as the rapidity and degrees to which they are degraded [5]. There are several methods that have been used in the long-term measurement of CO_2 evolution rates. One of the oldest yet simplest methods for estimating the rates of CO_2 evolution is a titrimetric analysis for CO_2 trapped in an aqueous alkali solution [6].

Experimental Objective and General Procedures

The overall objective of this research was to set-up bench-scale reactors designed to quantify the amount of microbial respiration produced in the biological decay of diesel fuel and gelled diesel-fuel in two common southern New Mexico soils. The measurement of the CO_2 released through respiration would indicate the degree to which the materials were biodegradable and CO_2 evolution rates, attributable to living, metabolically-active microbial-cells in the soil, would determine the rapidity and degree to which to which the contaminants were mineralized.

The experimental procedure used in this research was adapted from Procedure 41-3.2.4 of the Methods of Soil Analysis, Part 2, Chemical and Microbiological Processes [5]. Approximately 50 grams of randomly sampled soil (including the appropriate amount of contaminant and water) was placed in an air-tight reactor and 30 mL of 0.25N NaOH solution was placed above the soil surface in an open jar (alkali trap). The soil reactor and alkali trap are shown in Figure 3. As CO_2 evolves from the soil surface, it is trapped within the reactor and confined until it can diffuse or be absorbed by the NaOH solution [5]. After a period of time, the NaOH solution was removed from the reactor and the amount of CO_2 evolved was determined by titration with a 0.25N solution of HCl. Following the titrations, the soil in each jar was mixed, the alkali traps refilled with NaOH and the reactors set aside for a period of time until another set of readings were to be taken. Cumulative CO_2 evolution values were calculated in mg of CO_2 evolved per kg of dry soil.

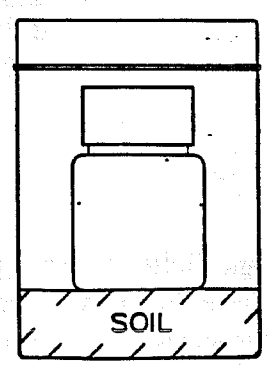

Figure 3. CO_2 Evolution Soil Reactor and Alkali Trap

Test Abbreviations and Contaminant Conditions

The following abbreviations were used throughout the test: Bl = Blank, no contaminant added; D = diesel fuel added to the soil test reactor; and GD = gelled diesel-fuel added to the soil test reactor. In each of the diesel fuel contaminated (D) test reactors, 7.5 mL of diesel fuel was added to 50 g of dry soil (120,000 mg diesel/kg of dry soil). For the gelled diesel-fuel contaminated (GD) test reactors, 7.5 mL of diesel fuel was added to 2.0 g of Enviro-Tech 410 and allowed to solidify. Following solidification, the gelled diesel-fuel was broken into small pieces and incorporated into the soil (120,000 mg gelled diesel-fuel/kg dry soil).

Soil Samples

Two common southern New Mexico soils were used in this study. One of the soils was characterized as an agricultural soil well suited for nut crops and was classified as a mixture of Harkey clay loam (Hk), Glendale clay loam (Gf), and Glendale loam (Ge). The sandy desert soil is typically found in the Rio Grande Valley and was classified as a Bluepoint loamy sand (Bm). Prior to the set-up of the degradation experiment the following preliminary soil treatments and analyses were conducted: all large cobbles, twigs, and other such debris were removed using a 1/4" sieve; standard ASTM sieve analyses [7] and moisture content determinations [8] were conducted; organic carbon, nitrogen, and phosphorus concentrations were analyzed; and a standard pressure-plate analysis was performed [9].

Soil-Water Conditions Tested

Results of the pressure plate analysis provided information for the development of soil-water curves. Field capacity (FC) for both soils was assumed to occur at approximately 0.25 bars and from the soil-water curve, the moisture content (MC) corresponding to this pressure was easily obtained. Three different soil-water conditions were examined; 30, 60, and 90% of the soil FC (90% of the FC is the wettest soil-water condition and 30% of the FC is the driest soil-water condition). Subsequently, the soil-water curves were again used to determine the MC that corresponded to the aforementioned soil-water conditions. The MCs for the following soil-water conditions are summarized below:

Soil	30% of FC	60% of FC	90% of FC
Agricultural	17%	20%	24%
Desert	7%	9%	11%

DISCUSSION OF RESULTS

Biodegradability of Diesel Fuel and Gelled Diesel-Fuel

In order to determine if diesel fuel and gelled diesel-fuel were biodegraded in the agricultural and desert soil reactors, CO_2 evolution rates for the contaminated soils were compared with the CO_2 evolution rates of the uncontaminated soil. The results of this comparison are summarized in Table 1.

Table 1
Average CO_2 Evolution Rates, Average Percent Changes in Evolution Rates, and Average Diesel Fuel Degradation Rates for Uncontaminated (Bl), Diesel Fuel Contaminated (D), and Gelled Diesel-Fuel Contaminated Agricultural (Ag) and Desert (De) Soils.

Soil/ID	Average CO_2 Evolution Rate (mg CO_2/kg-d)	Average Percent Increase from Uncontaminated (Bl) Reactor	Average Diesel Degradation Rate (mg diesel/kg-d)
Ag/Bl	10.8	----	----
Ag/D	77.1	686	24.5
Ag/GD	84.4	746	26.8
De/Bl	3.41	----	----
De/D	37.5	992	11.9
De/GD	34.3	896	10.9

The results show that the CO_2 evolution rates for the contaminated soils (D and GD) are markedly higher than the those in uncontaminated soil (Bl). The conclusion can be made that the large increases in the CO_2 evolution rates in the contaminated soils are attributed to microorganisms present in the soil that are capable of degrading diesel fuel and gelled diesel-fuel. These results are shown graphically in Figure 4 which illustrates cumulative CO_2 evolution curves for both soil types at a soil water content of 90% of FC.

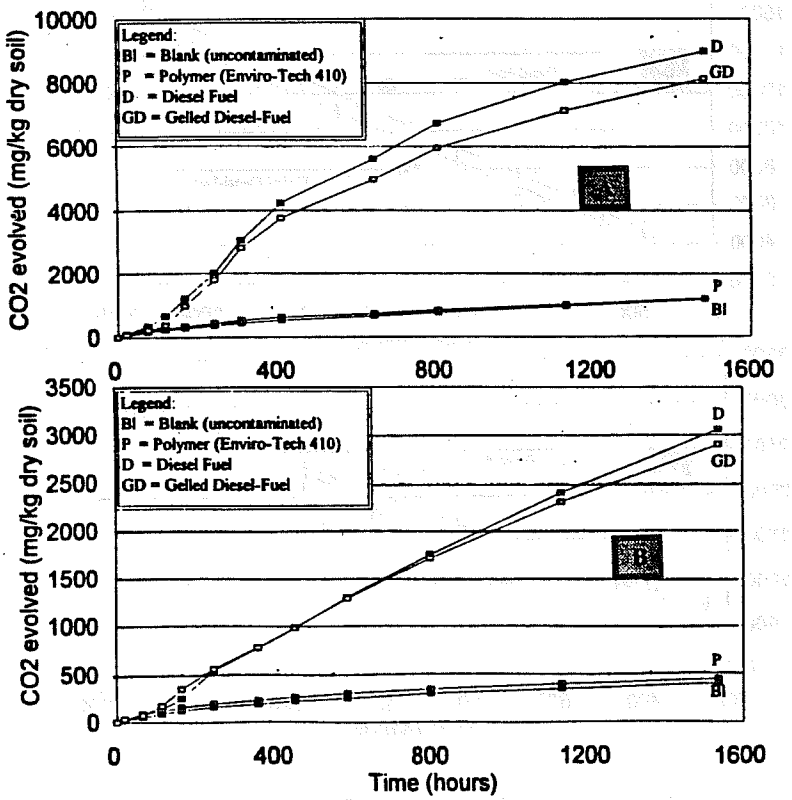

Figure 4. Cumulative CO_2 Evolution in Agricultural (A) and Desert (B) Soils.

In addition, Table 1 shows that average diesel fuel (or gelled diesel-fuel) degradation rates are approximately 2 times higher in the agricultural soil than in the desert soil. The following are a few possible explanations for this phenomenon: (1) there may be a more extensive, numerous, and diverse population of hydrocarbon-degrading soil microorganisms in the agricultural soil; (2) the microorganisms indigenous to agricultural soil may be more efficient at degrading diesel fuel than the microbes indigenous to desert soil; and (3) the desert soil may have a limiting factor, possibly soil nutrients, which has a negative effect on the degradation process.

Statistical Comparison of Diesel Fuel and Gelled Diesel-Fuel Contaminated Soils

The results discussed in the previous section verify that both the diesel fuel and the gelled diesel-fuel are biodegradable. However, these results do not show that gelled diesel-fuel is as biodegradable as diesel fuel or vise versa. In order to make an appropriate comparison, a statistical analysis was conducted to compare the CO_2 evolution rates for diesel fuel and gelled diesel-fuel contaminated agricultural and desert soils. The statistical analysis used for this comparison required the construction of a "best fit" line from a linear regression of the actual CO_2 evolution data points and determination of 99% confidence level limits. Figure 5 (A and B) shows the 99% confidence level error brackets for the CO_2 evolution curves for diesel fuel and gelled diesel-fuel contaminated soils at a soil-water condition of 90% of FC.

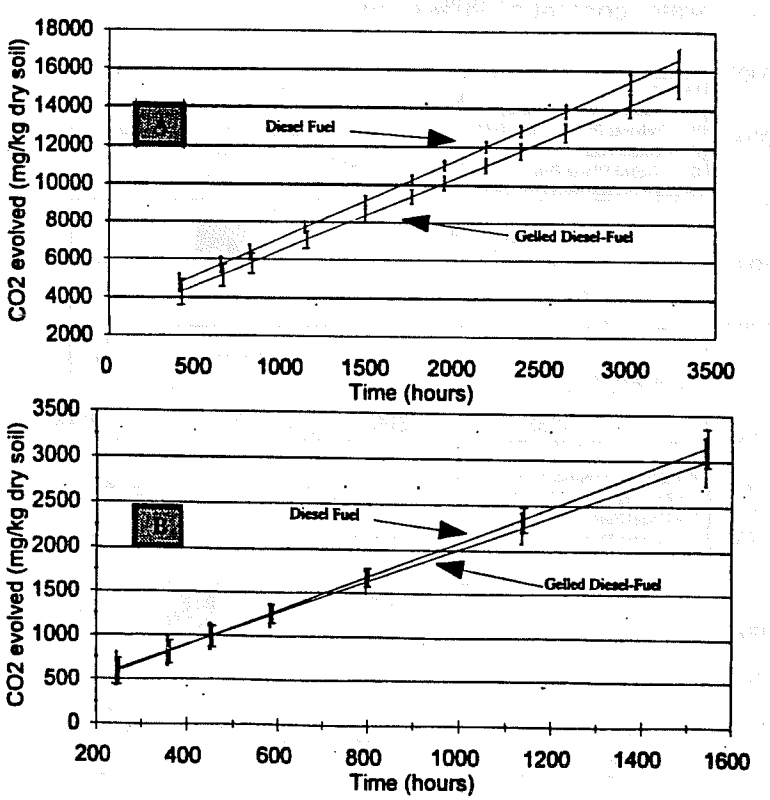

Figure 5. 99% Confidence Level Error Envelopes for "Best Fit" Line of Cumulative CO_2 Evolution in Diesel Fuel and Gelled Diesel-Fuel Contaminated Agricultural (A) and Desert (B) Soils.

In both cases (A and B) the error envelope brackets overlap which suggests that at a 99% confidence level the CO_2 evolution curves are statistically similar. In essence, this shows that at the 99% confidence level, there is no statistical difference between the degradation rates of diesel fuel and gelled diesel-fuel in agricultural and desert soils at soil-water contents of 90% of FC and implies that in soils similar to the ones used in this study, gelled diesel-fuel would be as biodegradable as diesel fuel.

Effect of Soil-Water Content on CO_2 Evolution Rates

The water content of soils is often described in terms of FC, which is a term that defines the state of the soil following the drainage of gravitational water. At FC, the micro- or capillary pore spaces of the soil are still filled with water that is available for microbial growth [10]. Soil-water content is a major factor in the degradation of petroleum contaminants. Without sufficient moisture in the soil, the contaminant does not become solubilized and in effect is not available to the soil microorganisms. Therefore it seems logical that soils with greater, more ideal MCs would experience higher CO_2 evolution rates (higher contaminant degradation rates).

In this study the soil moisture was amended to a MC that represented a certain percentage of the MC of the soil at FC. Figure 6 shows the effects that soil MC has on the cumulative CO_2 evolution rates of agricultural and desert soils contaminated

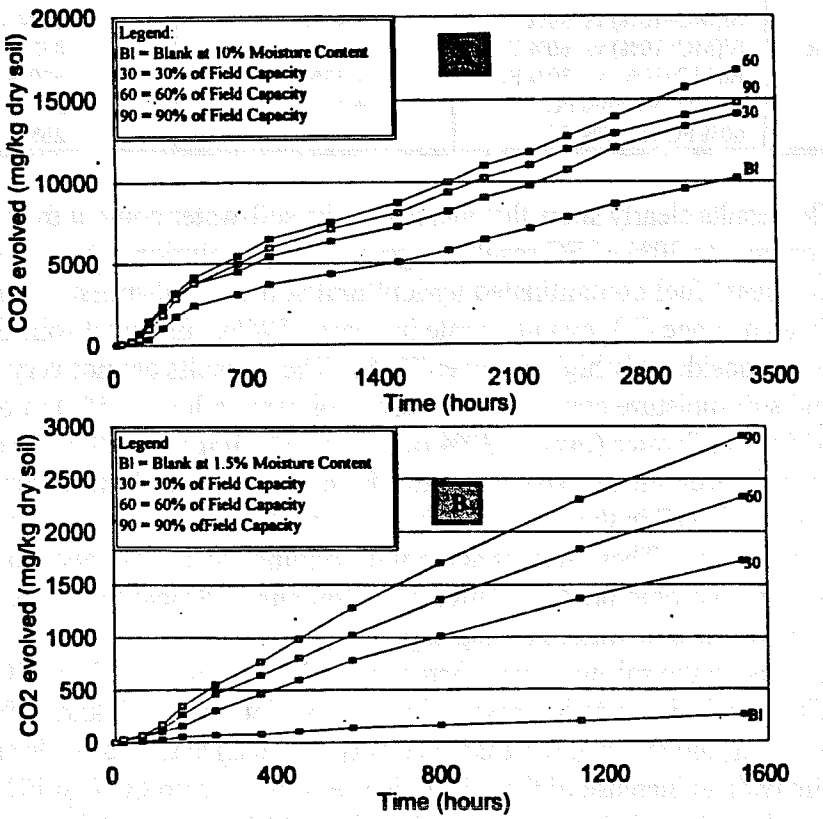

Figure 6. Cumulative CO_2 Evolution in Agricultural (A) and Desert (B) Soils Contaminated with Gelled Diesel-Fuel at Varying Soil Moisture Contents.

with gelled diesel-fuel. The CO_2 evolution curves for diesel fuel contaminated soils are very similar to the ones shown in Figure 6. As evidenced in Figure 6, there is a trend that shows increasing CO_2 evolution rates accompanied by increased soil-moisture content.

In order to quantify the differences between the various moisture conditions, percent increases (or decreases) in CO_2 evolution rates were calculated. This was done by comparing the CO_2 evolution rates for moisture amended soils to the rates observed in the soils that did not receive additional moisture. Table 4 provides a summary of the CO_2 evolution rate data at varying soil-moisture contents.

Table 4
Summary of the CO_2 Evolution Rate-Changes for Various Changes in Soil-Moisture Content in Agricultural and Desert Soils

Contaminant	Change in Soil-Water Content/Condition	Resulting % Change in CO_2 Evolution Rates in Agricultural Soil	Resulting % Change in CO_2 Evolution Rates in Desert Soils
Diesel Fuel	Bl(MC=10%) vs. 90% FC	+ 58%	+ 1390%
	Bl(MC=10%) vs. 60% FC	+ 34%	+ 1085%
	Bl(MC=10%) vs. 30% FC	+ 19%	+ 811%
	30% FC vs. 60% FC	+ 13%	+ 30%
	60% FC vs. 90% FC	+ 18%	+ 26%
Gelled Diesel-Fuel	Bl(MC=10%) vs. 90% FC	+ 41%	+ 1124%
	Bl(MC=10%) vs. 60% FC	+ 57%	+ 872%
	Bl(MC=10%) vs. 30% FC	+ 33%	+ 620%
	30% FC vs. 60% FC	+ 18%	+ 35%
	60% FC vs. 90% FC	- 11%	+ 26%

The results clearly show that increasing the soil-water content from its natural moisture content to 30% of FC results in greater CO_2 evolution rates. In diesel fuel and gelled diesel-fuel contaminated agricultural soil the soil-moisture amendment resulted in an average CO_2 evolution rate increase of 26%. In desert soils the average increase was considerably higher at over 700%. These results are not very surprising. The natural soil-moisture content of the desert soil was so low (1.5%) to begin with, that the addition of water (even at 30% of FC) greatly improved the soil conditions and led to enhanced biodegradation rates. It appears that for both agricultural and desert soils, a soil MC in the range of 60% of FC to 90% of FC would be the optimal soil-water condition. These results agree with findings of Dibble and Bartha which showed that the aerobic biodegradation of petroleum hydrocarbons was greatest at 50% to 70% of the soil water holding capacity [11].

Increasing the soil-moisture content from 30% of FC to 60% of FC results in average CO_2 evolution rate increases of 16% in agricultural soil and 33% in desert soils. However, the average increases are only 4% in agricultural soils and 26% in desert soils with an increase of the soil-moisture content from 60% of FC to 90% of FC. The highest degradation rates occur in soils at 90% of FC. However, increases in the soil-water content from 30% of FC to 60% of FC resulted in greater incremental degradation-rate increases than those observed when the soil-water

content was increased from 60% of FC to 90% of FC. This suggests that in a land application system, increasing the soil-moisture from 60% of FC to 90% of FC may not be critical. Minimal increases in the degradation rate afforded by the water addition would make this an unattractive option from an economical standpoint. Another concern is the greater possibility of leaching. As the soil-moisture content approaches field capacity, excess water in the soil pore spaces may be drawn through the soil by gravitational forces. This process, a direct result of high soil-moisture contents, may also cause leaching of the contaminant. Finally, increases in the soil-moisture content can inhibit oxygen availability and slow down the biodegradation process [11].

CONCLUSIONS AND RECOMMENDATIONS

The following list summarizes the conclusions and findings of this research:

- the agricultural and desert soils contain populations of soil microorganisms capable of degrading both diesel fuel and gelled diesel- fuel;

- the biodegradation of diesel fuel and gelled diesel-fuel is minimal in desert soils at a MC of 1.5% (natural, dry unamended soil state);

- the average degradation rates for diesel fuel and gelled diesel-fuel are approximately two times higher in agricultural soil (25.7 mg diesel/kg dry soil-day) than in desert soil (11.4 mg diesel/kg dry soil-day);

- at the 99% confidence level, it can be concluded that biodegradability of gelled diesel-fuel is statistically similar to the biodegradability of diesel fuel in both soils at a soil-water content of 90% of FC.

- increased degradation rates (as measured by CO_2 evolution rates) are associated with increases in the soil MC;

- increases in the soil-water from its natural MC to 30% of FC, resulted in average biodegradation rate-increases of 26% in agricultural soils and 700% in desert soils;

- increases in the soil-water from 30% of FC to 60% of FC resulted in greater incremental degradation-rate increases than those observed when the soil-water was increased from 60% of FC to 90% of FC;

- the results suggest that a soil MC on the order of 60% of FC will yield good biodegradation rates at landfarming facilities with soils similar to the ones tested in this study.

The results of this work indicate that both diesel fuel and gelled diesel-fuel are biodegradable petroleum-base products. Although the results are conclusive, there exists the need to upgrade and improve the testing methods from the bench-scale level to pilot- and field-scale as there is a lack of knowledge and operating parameters for biodegradation of organic pollutants in soil environments.

A more comprehensive study of the various soil and environmental factors that affect biodegradation of diesel fuel and gelled diesel-fuel by soil microorganisms would be highly recommended. The identification of optimal conditions for factors such as temperature, contaminant loading-rates, soil nutrient concentrations, soil pH, and tilling frequency is important for the design and operation of a land application facility.

It may also be of interest to conduct a study which would identify the microorganisms that are responsible for the degradation of the diesel fuel and gelled diesel-fuel in each soil. This may be accomplished by conducting plate counts and utilizing various specialized culture media to target and isolate specific microorganisms.

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Testing the Applicability of Soil Magnetic Susceptibility for Methane Detection at the Norman Landfill, OK

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ABSTRACT

The purpose of this study is to test whether soil magnetic susceptibility (SMS) is capable of indicating the presence of microseeping hydrocarbons generated at landfills. A core from the cap of the Norman Landfill in Oklahoma shows varying SMS with depth. Two distinct zones of elevated SMS are present in the core. The acquisition of an isothermal remanent magnetization (IRM) in samples from all zones reveal: 1) the dominant mineral is a low coercivity phase such as magnetite, and 2) elevated magnetic susceptibilities are caused by this phase. In a second study, the magnetic susceptibilities of samples from above a leachate plume adjacent to the same landfill were measured. SMS values decrease with increasing distance from the landfill. The SMS trend is consistent with the direction of migration of the plume as has been determined in other studies. IRM acquisition curves from samples along a representative transect, however, show no differences in magnetic mineralogy. Results of grain size analyses revealed a strong correlation between abundance of mud (< 63 microns) and SMS. The decrease in magnetic susceptibility with distance from the landfill can therefore be explained by gradually decreasing amounts of mud and may not be related to the leachate plume. Future work will focus on identifying the magnetic mineral causing the trends and the mechanisms responsible for causing the differences in magnetic susceptibility.

INTRODUCTION

The magnetic properties of soils and sediments develop in a dynamic system and reflect natural pedogenic processes, both inorganic and biologic, as well as cultural influences in the form of anthropogenic chemical influxes. Several researchers have found that microseepage of hydrocarbons from reservoirs can cause anomalous increases in the magnetic phases in soils which can be detected by measuring soil magnetic susceptibility (SMS) (1). SMS surveys have been successfully used as a rapid and cost effective petroleum exploration tool (2). The objective of this study is to test SMS as a tool to detect microseeping hydrocarbons (e.g., methane) at, and around landfills. Two studies have been performed at an abandoned landfill in Norman, Oklahoma. Samples were collected from a core in the landfill cap and from above a known contaminant plume emanating from the landfill.

SMS could offer an attractive alternative to other geophysical, or biologic characterization techniques. SMS surveys may provide rapid, noninvasive, and cost effective assessment of hydrocarbon/metal contamination and bioremediation processes.

BACKGROUND

Magnetic susceptibility

Magnetic susceptibility is capable of measuring differences in the content of magnetic material(s) within soils, sediments, and rocks. High values of magnetic susceptibility might indicate the addition of magnetic material by chemical or biochemical processes. However, differences in magnetic susceptibilities can also be a result of variations in soil/sediment type, changes in the grain size of the magnetic minerals, or alteration to other magnetic phases. The most common magnetic minerals found in soils and sediments include iron oxides such as magnetite and maghemite, and iron sulfides such as pyrrhotite and greigite (3).

Hydrocarbon seepage and magnetic anomalies

Numerous studies have documented a relationship between hydrocarbons and precipitation of authigenic magnetite. For example, several researchers (4,5) report a connection between authigenic magnetite and biodegraded hydrocarbons from surface seeps. Key evidence for the hypothesized connection comes from studies of hydrocarbon-saturated calcite speleothems (4,6). Speleothems with hydrocarbons contain a remanent magnetization in magnetite whereas speleothems without hydrocarbons do not contain a stable magnetization. The intensity of the magnetization is apparently related to the amount of hydrocarbons present in the speleothems and the chemical conditions created by the hydrocarbons caused the magnetite to form (7).

A number of other workers have proposed that magnetic minerals (generally magnetite) produced during hydrocarbon microseepage can be regarded as "fossil" indicators of seepage and that SMS may be used as an inexpensive and efficient method for petroleum exploration (2,8,9). Recent studies have found a significant correlation between shallow hydrocarbon productions and soil magnetic susceptibility (1,10,11). Sampling vertical profiles, both above and away from oil production suggests that a magnetic anomaly is largely concentrated in the organic rich "A" soil horizon (Figure 1). Mineral identification by Curie balance indicates the presence of magnetite in samples over producing fields (10).

Soil magnetic susceptibility (SMS) anomalies have been documented at a landfill and the anomalies have been related to methane production in the landfill (12). The mechanism of the magnetic mineral formation in the circumstances described above has not been elucidated. Changes in hydrocarbon composition and the stable isotope fractionation patterns suggest a connection with hydrocarbon biodegradation (7).

Mechanisms of magnetic mineral formation

The magnetic minerals in soils or sediments can be present at deposition or can be formed by different processes after deposition. For instance, the results from a number of studies suggest that the chemical conditions created by hydrocarbons can cause precipitation of the authigenic magnetite (5,7,13-15).

Other workers (16-18) describe the chemical conditions that can cause magnetite and other magnetic phases to form (e.g., low oxidation potential, low sulfur, and intermediate total inorganic carbon content). Machel and Burton (16) also point out that magnetic phases can form as a result of kinetic and/or microbial effects.

The hypothesis that microorganisms metabolize hydrocarbons has been described as one possible diagenetic pathway that might contribute to the formation of authigenic (secondary) magnetite (4,5). Evidence from several studies suggests that various biological factors play significant roles in the formation of several magnetic minerals including magnetite (19-23). A variety of microorganisms are capable of producing magnetic minerals either directly or indirectly. Among those bacteria are dissimilatory Fe(III) reducers (24-27), magnetotactic bacteria (28-30), and sulfate-reducers (31,32). Although laboratory studies clearly show that microorganisms have the potential to change the properties of SMS in a wide range of environments that contain both hydrocarbons and metals, it is not clear whether biotic processes are important or even involved in the formation of SMS anomalies.

STUDY AREA

The Norman Landfill is an abandoned waste deposit site which is located south of the city of Norman in Cleveland County, Oklahoma and is approximately 400 m north of the current position of the South Canadian river (Figure 2). The landfill was utilized as a legal disposal facility for municipal wastes from 1922 to 1985. Between 1985 and 1989, the landfill was covered and completely capped with a clay-rich soil type (33). The cap had an initial thickness of at least ninety centimeters and was covered with topsoil to establish vegetation. The capping material was taken from the north campus area in Norman which is a few miles distant from the landfill.

South of the West Cell (Figure 2) a contaminant plume had been detected in the subsurface within a shallow aquifer (34). The plume is migrating towards the South Canadian River. In the recent past several research groups have described characteristics of the contamination including microfauna and chemistry (35) whereas others have mapped its position using different methods (36). Beeman and Suflita (37) reported the presence of methanogenic microorganisms in the plume area. The area is mostly characterized by a relatively dense vegetation cover. Mostly present, but not ubiquitous, is a very thin topsoil layer that overlies an approximately 20 to 30 cm thick deposit of a flood event which consists mainly of clay and silt. This flood layer is limited in the east by the East Cell of the landfill, in the south by an abandoned channel of the river, and in the west by the reworking of material by an asphalt company. A layer of dominantly coarse sand deposited by the river is present below the flood deposit.

METHODS

A core, retrieved from the landfill cap at the south side of the West Cell (Figure 2), was collected in a non-magnetic tube. The core lithology was described and samples collected. In order to sample above the contaminant plume, an orthogonal grid was set up prior to sampling south of the West Cell (Figure 2). A total of 254 samples above the plume area were retrieved at a depth of 20 cm from within the flood deposit. Potential contamination with magnetic materials during sampling was avoided by using non-metallic tools. Control samples were taken from the original location of the capping material and from a flood deposit on the south side of the Canadian River.

All samples were weighed and their magnetic susceptibilities were measured in mass units immediately after returning from the field to avoid possible changes in the magnetic mineralogy due to the removal of the samples from their original chemical environment. Magnetic susceptibilities were measured three times using a Sapphire Instruments SI-2 system. After a period of two months, SMS measurements were repeated for the samples to determine whether any changes had taken place. The SMS was found to be unchanged. The samples taken

along the transects south of the West Cell and the control samples were air dried for 15 days at room temperature. The original SMS measurements were used to calculate the weight normalized SMS applying the dry material weight.

Soil samples from the core, transect, and both control locations were placed into an impulse magnetizer to measure their acquired isothermal remanent magnetization (IRM). The samples were subjected to increasingly higher applied magnetic fields and the remanence was subsequently measured in a 2G cryogenic magnetometer. Examination of IRM acquisition curves is capable of identifing magnetic minerals based on their coercivity spectra.

Multiple samples along one representative transect above the plume area and a sample from the other side of the river were analyzed for their grain sizes. Distilled water was mixed with 2.55g of sodium-hexametaphosphate per liter to prevent clays from clustering. For each sample a small amount of material (less than 15 g wet weight) was treated with the mixture for at least 18 hours. By wet-sieving each sample through a 63 microns sieve (USA standard mesh 230) the coarse fraction (sand) was separated from the fine fractions. To find the exact dry weight percentage of the mud fraction (< 63 microns), pipette analyses were performed (38). All samples were dried in an oven at approximately 114 °C for at least 25 hours. Their dry weights were measured and the mud weight percent was calculated for each sample.

RESULTS AND INTERPRETATIONS

Landfill Cap

The core shows two distinct layers below a thin cover of topsoil. The upper 68 cm consist of the actual capping material (Figure 3, indicated as mud). Below the mud is a 26 cm thick layer consisting of coarse sand which is partly mixed with waste particles. Figure 3 shows the results of the downcore magnetic susceptibility measurements as well as those of the background. There are three distinct zones of magnetic susceptibility within the mud layer. Zone I has magnetic susceptibility values that are elevated relative to the background samples and show a decreasing trend with increasing depth. A second zone has magnetic susceptibility values that are similar to the natural SMS of the control samples. Zone III, which is found at 50 to 68 cm depth, again has augmented SMS relative to the control samples.

The acquisition of IRMs in representative samples from each zone and the background indicate the presence of at least two magnetic phases in all of the samples. The steep increase in remanent magnetization at low applied magnetic fields (up to 200-250 mT) suggests the presence of a low coercivity mineral, such as magnetite (Figure 4a). The continuous gradual increase in remanence above

200-250 mT is indicative of a high coercivity mineral, in this case most probably hematite. The shapes of the normalized IRM curves (Figure 4a) at low applied magnetic fields are very similar for the control sample and a sample taken from zone II, both of which have comparable magnetic susceptibilities. This suggests similar ratios of the low versus high coercivity minerals. The slope of the curves at low applied fields for samples from zones I and III are steeper compared to the slopes in the background and zone II curves. This indicates that the ratio of low to high coercivity phases has increased. The magnetic intensity of the IRM at 200 mT (Figure 4b) is higher for samples from zones I and III compared to zone II and the background samples. This indicates that there is more of the low coercivity mineral in samples from zones I and III.

Leachate plume area

Magnetic susceptibilities of samples from the flood deposit above the leachate plume show a decreasing trend with increasing distance from the landfill (Figure 5). This trend is consistent throughout all transects within the plume area. The trend in SMS coincides with the direction in which the plume is migrating. A similar flood deposit on the north side of the river contains magnetic susceptibility values that are similar to samples with high SMS values near the landfill (Figure 5). Normalized acquisition curves of four selected samples from along a transect and a control sample are displayed in figure 6. A low and a high coercivity mineral are present within all samples. The almost identical appearances of all the normalized IRM curves suggest that the magnetic mineralogy and relative abundances of the magnetic phases is the same in the samples.

Grain size analyses of representative transect samples and a control sample show a strong correlation between sediment size and magnetic susceptibility with a regression coefficient of 0.96 (Figure 7). Samples closer to the landfill have a higher content of fine grains and higher SMS. As the content of mud decreases with increasing distance from the landfill, the magnetic susceptibilities also decrease.

DISCUSSION AND CONCLUSIONS

Landfill Cap

The elevated SMS in zone I compared to the SMS in control samples suggests the possible addition of magnetic material. Comparison of the IRM acquisition curves suggests a low coercivity mineral has been added to zone I. This increase in low coercivity magnetic material in zone I may have been caused by soil processes which can form inorganic magnetite (39). Methane emanating from the landfill could theoretically cause the susceptibility high, but if this is the case then it is difficult to explain why the SMS within zone I decreases with increasing depth.

Magnetic susceptibilities of samples in zone II are very similar to those of the control samples suggesting that there are no differences in the abundance of magnetic phases. Similar IRM acqusition curves for zone II and background samples show no evidence that growth or destruction of a magnetic phase occurred in zone II. This zone is apparently unaffected by the process(es) that cause elevated magnetic susceptibility in the surrounding zones.

Magnetic susceptibilities and acquired remanence in samples from zone III are similar to those of zone I. A low coercivity mineral has been added to the samples which apparently accounts for the elevated SMS. The creation of a low coercivity phase such as magnetite within zone III is consistent with the proposed hypothesis that methane emanating from the landfill can cause an increase in SMS. Soil magnetic susceptibility, therefore, may be capable of tracing landfill-generated methane. To support this conclusion, it is necessary to conduct additional rock magnetic experiments to uniquely identify the authigenic phase created in zone III of the landfill cap. Microbiological investigations will test for a possible biogenic origin for the authigenically formed low coercivity mineral.

Leachate Plume Area

The decrease in magnetic susceptibility decreases with distance from the landfill is consistent with a model where less methane-derived magnetite is being created as a result of plume dilution. The results from the control samples and the IRM acquisition experiments, however, do not support the hypothesis. The magnetic susceptibility values for the control samples are similar to the higher values from the transect samples. The control samples are apparently not effected by contamination and therefore should not have elevated SMS. It should be noted, however, that it is not clear that the layer collected as background and the flood deposit adjacent to the landfill are the same and whether a comparison is valid. The similarities in the IRM acquistion curves also do not support the hypothesis that a magnetic phase has been added. If methane is being generated in the leachate plume, either it is not causing formation of magnetic minerals that can be detected or its effects are masked by grain size differences inherent in the flood deposit. It is possible that despite the fact that the flood layer is underlain by a highly porous and permeable sand, methane may not have migrated through all parts of the mud layer and its effects may therefore not be recognizable within the deposit. Additional studies are needed to determine why high SMS values are associated with high mud content and to identify the origin of the low coercivity phase within the contaminated area.

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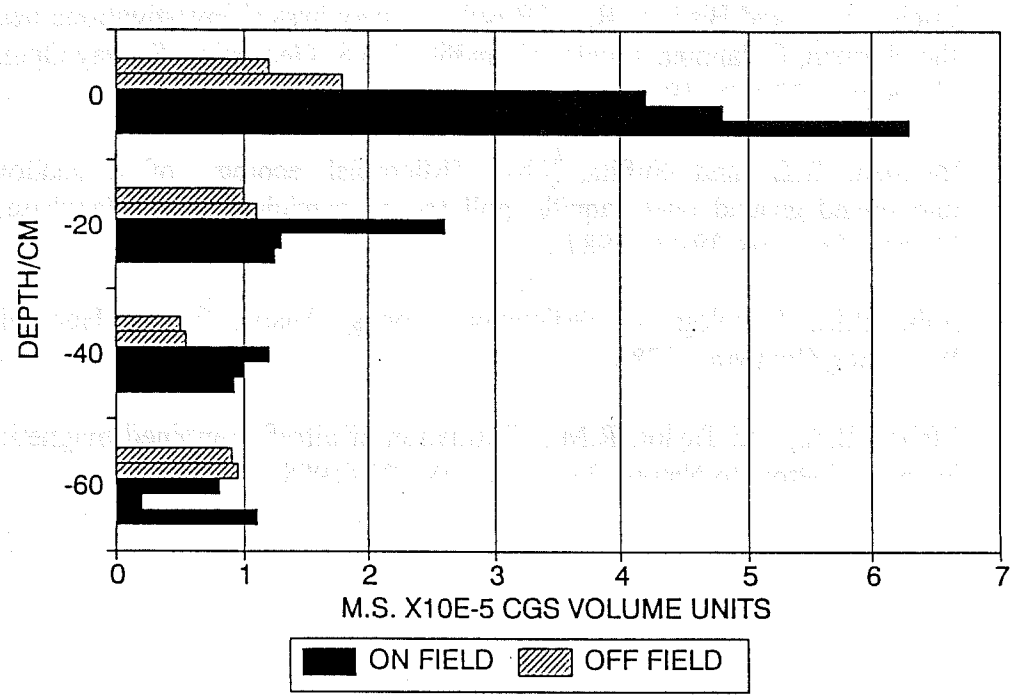


Figure 1. Magnetic susceptibilities of vertical soil profiles from both on and off gas fields in Cotton and Stephens counties, Oklahoma.

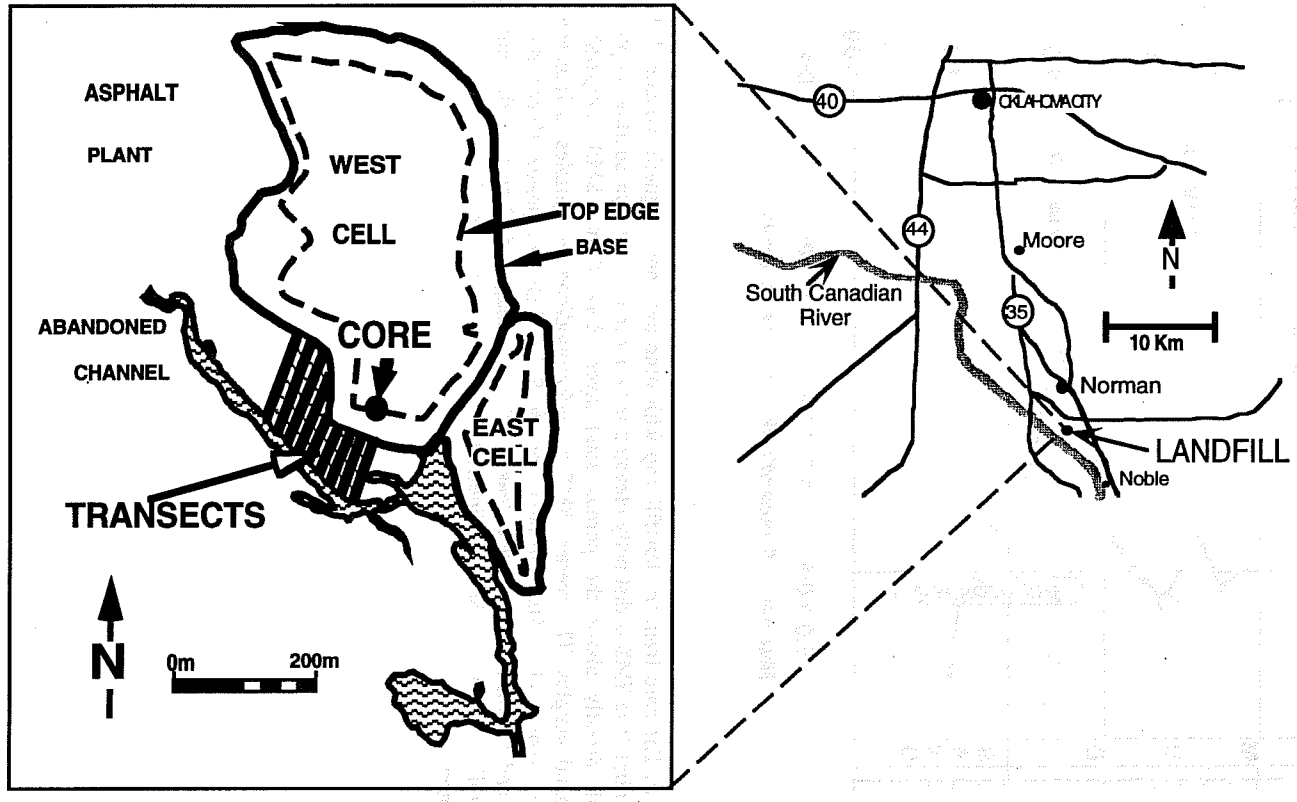


Figure 2. Map showing the location of the Norman Landfill in Oklahoma, with an enlargement of the study site. The position of the core on top of the cap and the transects above the plume area are also indicated.

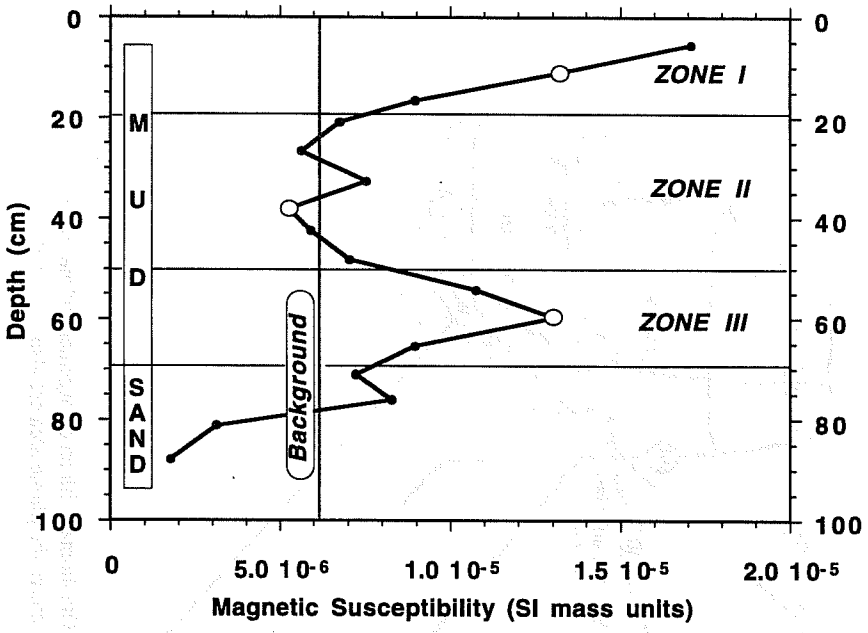


Figure 3. The core from the landfill cap with lithology and magnetic susceptibilities (mass units). The SMS is distinctly elevated in two zones, zone I at shallow depth, and zone III, directly above the porous sand layer. Zone II has SMS comparable to background samples. The average SMS of background/control samples is indicated by the black vertical line. Standard deviation for SMS of all data points (black dots and circles) and control samples were at least one order of magnitude less than the magnetic susceptibility measured. Samples indicated as circles were used for IRM acquisition experiments.

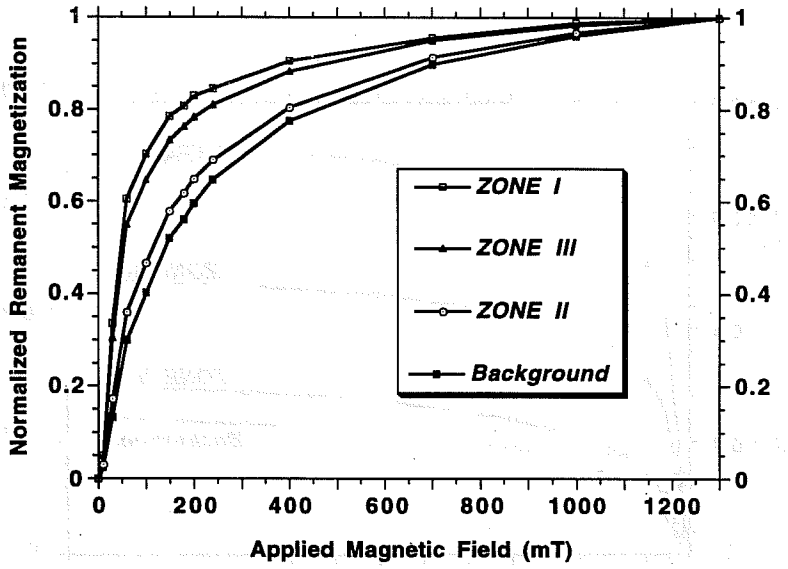


Figure 4a. Acquisition curves of isothermal remanent magnetization (IRM), normalized by their maximum remanent magnetization, of samples from zones I, II, III, and a control sample. Two minerals are present in all samples, a high and a low coercivity mineral. The slopes of the curves for samples from zones I and III are similar which suggests comparable ratios of the two minerals. A sample from zone II has a curve that is similar to the curve from the control soil.

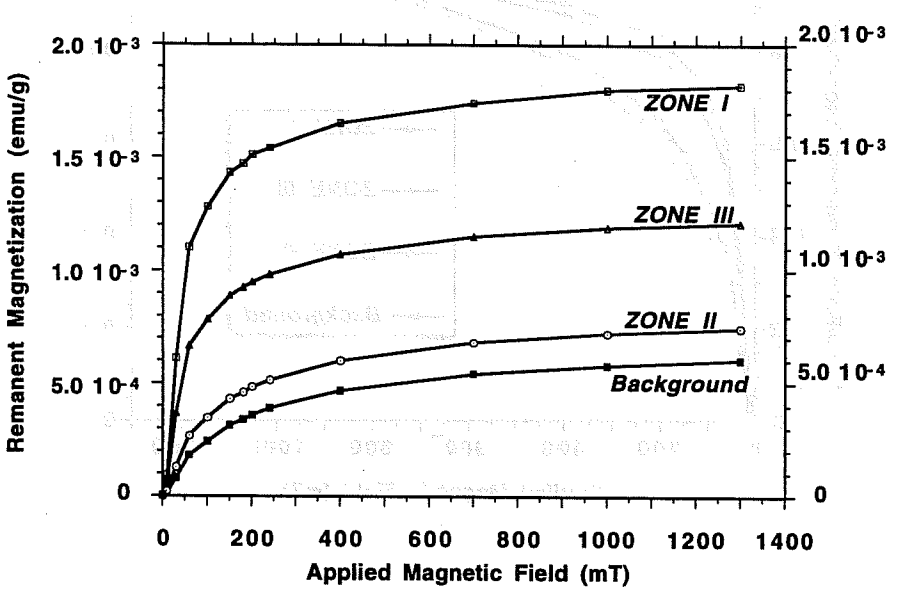


Figure 4b. Isothermal remanent magnetization acquisition curves showing the absolute values of the remanent magnetization for samples from zones I, II, III, and a control sample. The low coercivity phase (saturated at approximately 250 mT) is more abundant in samples from zones I and III compared to zone II and the background.

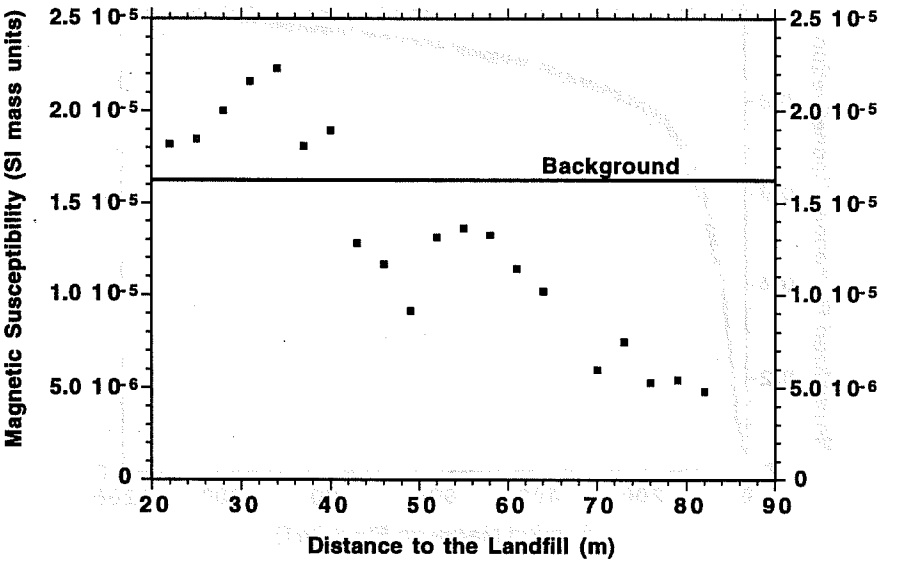


Figure 5. Soil magnetic susceptibilities (SMS) measured along a representative transect above the leachate plume adjacent to the landfill, and average SMS of background samples (horizontal line). SMS are decreasing with increasing distance from the landfill. Standard deviations for the magnetic susceptibilities are at least an order of magnitude smaller than the SMS measurements.

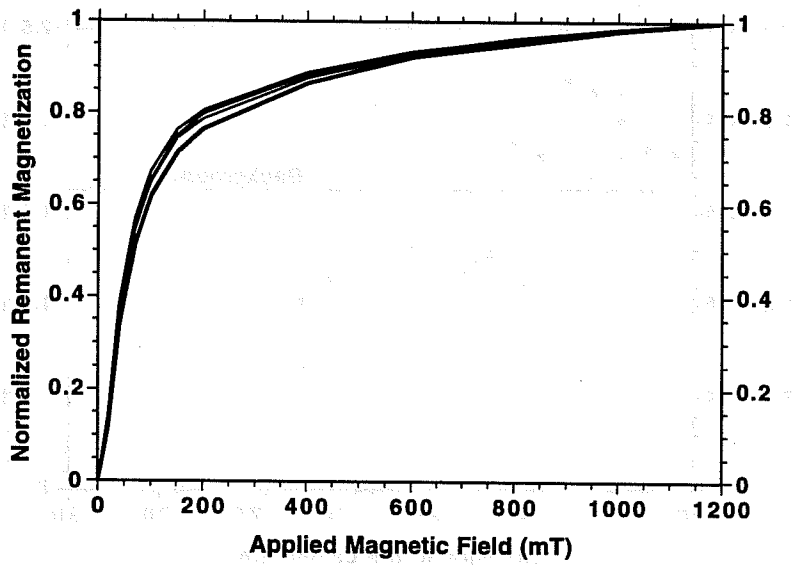


Figure 6. IRM acquisition curves for several samples from along a representative transect above the plume, and a background sample. The IRMs are normalized by each samples maximum remanent magnetization. All samples contain two magnetic phases: a high and a low coercivity mineral. The similarity of the curves suggests that the ratio of the two phases within the samples are the same.

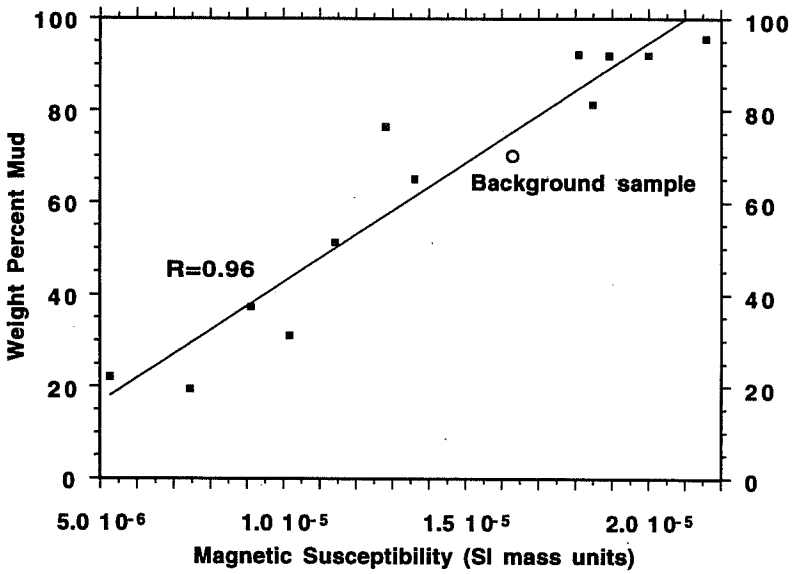
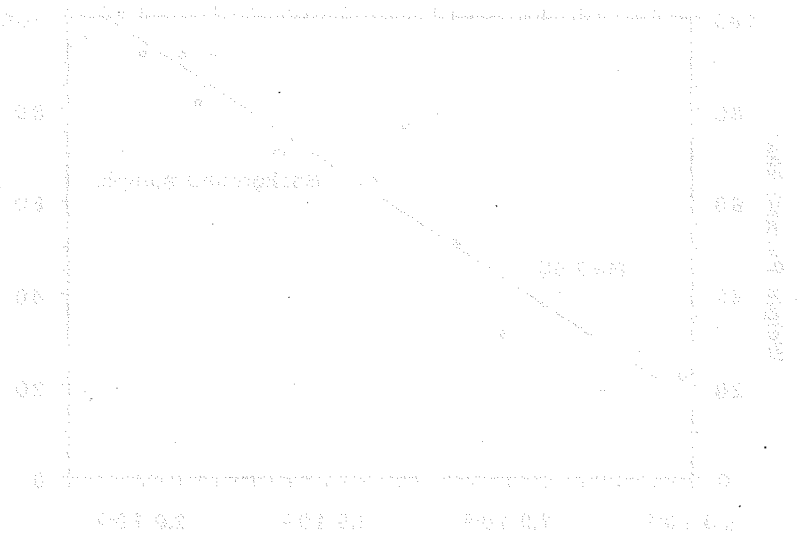


Figure 7. The weight percentage of mud plotted versus the magnetic susceptibilities of a control (background) sample and samples from the transect. SMS increases linearly with increasing mud content. A best fit line with a regression coefficient of R=0.96 is shown on the graph.



Determining the Age of Hydrocarbon Fuel Spills

Using Organic Geochemical Data

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Depending on the fuel-type spilled and site characteristics available, different approaches can be used to estimate time of a fuel release. These approaches are generally based on one of the following: (1) regulation dictated changes in the type and amount of additives blended to the fuel; (2) rate of compositional changes in fuel with time; and (3) changes in fuel components concentration with distance from the source of release. The compositional changes in environmental samples can be monitored using selected parameters calculated for different hydrocarbon classes. Among the most important parameters are the certain concentration ratios of individual BTEX hydrocarbons, n-C_{17}/Pr ratio and the selected PAH ratios. Documented history of lead additive and oxygenate composition, concentration and usage in gasoline makes them valuable time markers. Available site hydrology and fuel compound mobility data, allow for the time of a release estimate using contaminant transport simulation models.

This presentation describes a set of chemical tests developed to evaluate key parameters for various homologous series of hydrocarbons including alkanes, cycloalkanes and aromatic compounds. It also demonstrates how different approaches have been used for fuel-type identification and to estimate time of fuel releases. Based on the comparison of chemical parameters in dispensed reference fuels with those in the subsurface environment, a scheme has been prepared to illustrate the relative degradation level of different fuels with a volatility range from gasoline to Bunker C oil. This scheme should allow one to relate fuel-specific compositional changes with the length of time a particular fuel has been in the subsurface environment.

INTRODUCTION

In recent years, contamination of soil and groundwater by petroleum products has become a serious environmental problem. The need for potentially responsible parties, and their insurance carriers, to determine liability for releasing the chemicals and consequently, for the cleanup of petroleum contaminants, has resulted in increasingly sophisticated analytical and interpretative approaches to identify sources of contamination. Because of extreme complexity of the composition of petroleum and petroleum related products, no single analytical method can be used to identify all of its important components in the environmental samples. Moreover, because petroleum is also a labile mixture, the composition of a product released into the environment begins to change almost immediately due to numerous biochemical and physical processes.

As a result of physical processes, hydrocarbon fuel in the subsurface environment is distributed among the following major phases:

- Fuel vapors as a component of soil gas
- Fuel sorbed to soil particles
- Liquid fuel in pore spaces of the soil particles
- Liquid fuel floating on the groundwater table
- Fuel dissolved in groundwater

The distribution of fuel constituents among these phases is constantly changing, as hydrocarbons or additives move between different phases at various rates under different controlling conditions. In the soil above the water table, gravity causes liquid fuel to migrate downward from the release source. The infiltrating liquid loses its most volatile components into the soil air and most soluble constituents to the water surrounding soil particles. Fuel components are also lost because of sorption and capillary retention. As the liquid fuel reaches the groundwater table, it first dissolves and after reaching saturation it begins to accumulate and spread out as a free phase floating product.

Hydrocarbons released into the environment will also be subject to biotic and abiotic weathering reactions in the soil/groundwater media. These processes act in concert, with the rate of transformation being related to the chemical composition of the fuel and the environmental factors including temperature, soil moisture, nutrients content, and the oxygen content. For soil, grain size and clay-type are important parameters.

Major abiotic reaction types include hydrolysis, dehydrogenation, redox and polymerization. These reactions are often closely related to microbial (biotic) transformations in the soil profile. Biotic weathering of a hydrocarbon fuel consists of two interdependent mechanisms: microbial concentration and biodegradation. These transformations are likely to occur stepwise, producing alcohols, aldehydes, and fatty acids in sequence (1).

For the above reasons, a combination of standard EPA methods, as well as elaborate geochemical methods for characterization of petroleum products (2) have been applied for environmental samples from sites where the character and source of contamination by petroleum-derived material is not obvious. For such examples, the use of forensic environmental chemistry can facilitate determination of the contamination source and its history.

ANALYTICAL PROCEDURES

A variety of geochemical methods for characterization of petroleum is used extensively in exploration and production operations for crude oil and natural gas. Many of them, especially those related to oil-oil correlations and the typing of condensates, are also applicable to environmental problems, such as investigation of fugitive fuel spills or natural gas leaks. The analytical procedures used are based on "wet" chemical techniques involving extraction, separation and preconcentration, as well as variety of instrumental methods. These procedures are designed to search for specific characteristics in each sample supplied for analysis. A decision "tree" based on initial results and available site-specific information dictates what additional measurements are to be made.

The methods commonly used for the forensic characterization of escaped petroleum-related products include the following analyses:

- Gaseous hydrocarbons in the C_1-C_5 range by gas chromatography (GC) with flame ionization detector (FID)
- Identification of major volatile hydrocarbons in the gasoline range, using high resolution GC/FID
- Volatile aromatic hydrocarbons, benzene, toluene, ethylbenzene, and xylenes (BTEX), using GC with photoionization detector (PID)
- EDB, EDC and alkyl lead speciation, using GC with electron capture detector (ECD)
- Oxygenated blending agents (alcohols and ethers), using two-dimensional GC/FID
- Dye additives by thin layer chromatography (TLC)
- Total lead and organic lead, using inductively coupled plasma spectrometry (ICP)
- n-Alkanes in the C_8-C_{33} range, along with specific branched-chain alkanes, using GC/FID
- Alkylbenzenes, alkylcyclohexanes and PAH hydrocarbons by gas chromatography-mass spectrometry (GC/MS)
- Polycyclic saturated hydrocarbons, such as steranes and terpanes (biomarkers), which are chemical fossils of the biological materials from which the petroleum was originally formed, by GC/MS
- Stable isotope ratios for carbon ($^{13}C/^{12}C$) and hydrogen (D/H), by dual collector isotope ratio mass spectrometry
- Trace metals, especially vanadium (V) and nickel (Ni), by ICP.

TIMING A HYDROCARBON FUEL RELEASE

Timing a fuel or crude oil releases is site-dependent and requires consideration of a wide set of environmental parameters. Among these parameters are fuel composition, selected soil characteristics, site hydrology, temperature, moisture content, permeability, and oxygen and nutrient availability. In some environments, these parameters favor fuel preservation. In others, local environmental conditions strongly alter the composition of the fuel and degrade it completely in a short period of time.

Two approaches can be taken to determine the approximate time of a release: either identify the composition of the fuels as a function of time, or identify additives that were only used during restricted time periods. An example of the former is the demand for reformulation of fuels that has been imposed during the early 1990's, such as the regulation that lowers the sulfur content of diesel No. 2 fuel to 500 ppmw. A second example is the use of oxygenates, such as MTBE or alcohols, to blend with gasoline, which was imposed in the early 1980's for the east coast, gulf and mid-west states and in the late 1980's on the west coast.

Changes in the type and amount of additives with time is another useful approach. For example, in the 1960's, ARCO used borates as additives to its gasoline for a restricted time. The lead additive content of gasoline was high before 1980 and decreased until the late 1980's, when it was phased out in most states (Figure 1). Whereas several different lead alkyls were used between 1960 and 1980, with total lead rising above 3 g/gal, the primary use of only TEL occurred after 1980, when the total lead content for gasoline dropped to below 1 g/gal.

The second approach to resolve the time of release of a fuel or crude oil is to determine the rate of change of certain parameters in different hydrocarbon classes. For light hydrocarbon fuels such as gasoline, evaporation and dissolution are the most important weathering processes. Several parameters control the rate of fuel volatilization, the most important of which is the vapor pressure of its hydrocarbon constituents. According to vapor pressure data (3), it requires approximately one month to remove n-butane from a silty soil saturated with gasoline by volatilization from a depth of 12 feet below soil surface, whereas n-octane still may be detected in the soil after more than 10 years.

Dissolution is another primary mechanism of gasoline weathering. Because of substantial differences in water solubility of gasoline components, water washing is important in altering the composition of the fuel. Under the environmental conditions stated above, the concentration ratio of benzene + toluene/ethylbenzene +xylenes in soil changes from about 0.8 in the original fuel to 0.4 after approximately five years. For fuel-contaminated groundwater this ratio in a dissolved hydrocarbon plume is also a useful parameter for time estimate. If the ratio falls between 1.5-6.0 near a suspected source, the spill is probably very recent, having occurred within the

last one to five years. This ratio will decrease exponentially as shown in Figure 2, because of the preferential removal of benzene and toluene, allowing the less soluble ethylbenzene and xylenes to increase in relative concentration (4).

Site hydrology can also provide additional means for estimating time of a release. When hydrocarbon fuel is dissolved in groundwater, it becomes part of a continuous, mobile phase. Mobility of different fuel hydrocarbons in this phase reflects their relative water-soil partitioning characteristics. Based on field studies conducted in unconfined sandy aquifers, benzene was estimated to have been transported at about 90% of the groundwater velocity, toluene at 75%, ethylbenzene and xylene isomers at about 67%, and MTBE migrated with groundwater flow without retardation (5). By monitoring changes in selected hydrocarbon and MTBE concentrations with distance from the source of a fuel release and using available mobility data from fuel components, it is often possible to estimate the time of a release.

Biodegradation is the major weathering process for heavy-end middle distillates and residual products released into the environment. Most commonly used parameters for measuring degree of biodegradation are the ratios n-C_{17}/Pristane, n-C_{18}/phytane and pristane/phytane.

Following the examination of several sites containing diesel fuel No. 2 in soil, where time of fuel releases had been documented, Christensen and Larsen (6) concluded that it was possible to estimate the length of time the diesel fuel had been in the environment by using the values of the n-C_{17}/Pr ratio. They obtained a linear relationship extending over a range of about 20 years, which can be approximated by the following equation

$$T(year) = -8.4 \frac{n\text{-}C_{17}}{Pr} + 19.8$$

Two other important parameters, that may be useful in determining changes of diesel fuel in free floating product and soil extracts, are also presented in Table 1. Changes in various hydrocarbon parameters in Bunker C fuel during biodegradation are shown in Table 2. All of these ratios are useful in estimating the degree of diesel and Bunker C alteration in the subsurface environment.

Based on the comparison of newly dispensed fuels with those in the environment, a scheme has been prepared (Figure 3) to illustrate the relative degradation level of different hydrocarbon types in fuels with a volatility range from gasoline to Bunker C fuel.

CONSTRAINTS ON ESTIMATING RELEASE TIME

The problems associated with timing of a hydrocarbon fuel release are compounded by a lack of reliable analytical data for sites with documented release dates. Described below are "extreme" situations in which estimation of a fuel release time is very difficult because of the soil composition and hydrologic controls.

- Bulk liquid phase fuel saturated soil. Bulk liquid hydrocarbons that coat soil particles are much less subject to environmental alteration, including biodegradation, than lower concentration hydrocarbons uniformly dispersed in soil or dissolved in water. This is because physical alteration processes mainly affect the interface and not the body of the bulk product. Biodegradation inside the body of a product is extremely slow because of the limitation of oxygen, water and nutrients. Although microorganisms which can survive in liquid hydrocarbon matrix are known, the rate of a product "spoilage" is low, because of the limitations described above. It is likely that a hydrocarbon fuel in such conservative environments can survive for a very long time (over 20 years in some cases) without detectable chemical changes in composition.

- Free phase floating product. When a thick layer (greater than six inches) of a free phase floating product develops on the groundwater surface, its rate of alteration significantly decreases. The reason for this is that the hydrocarbon fluid is immiscible with the groundwater. Alteration then occurs only at the interface of the fluid and the water below, or the fluid and the moist soil above the product. At the center of the free product layer, interactions with the ambient environment are likely to be exceedingly slow. Hence, if the free product fluid is rapidly transported to the water table and does not undergo substantial alteration during its vertical migration in the soil, it may remain in a relatively unaltered state for a period of time as long as several decades, depending on the thickness of the fluid and the dynamics of the hydrologic system. The most likely alterations which occur will be loss of vapors and loss of the most soluble hydrocarbons (BTEX), oxygenates (MTBE or alcohols) and the lead scavengers EDC and EDB.

  If a sample is collected from near the top or bottom of the fluid layer, there would be observable alteration by physical and biological processes. When a sample is taken from the center of a thick product layer, only minor amounts of alteration would be measured.

- Preservation of chemical properties by ultra fine-grained clays. When very fine-grained sediments dominate the soil composition, they are generally described as the clay fraction. This term is also applicable to specific mineralogic types which fall into the physical definition of clays. Examples for such clay types are kaolinites, illites, bentonites and smectites. The latter two are particularly important, in that they have large atomic lattice spacings, which cause the clays to swell, and they also have very large surface areas. Organic molecules and trace metals are known to strongly absorb on these

surfaces. Therefore, if these clays are present, porosity and permeability would be very low, restricting water migration through the soil and oxygen entry. Any fuels that entered the soil would be strongly adsorbed on the clays and would not alter rapidly, unless they are exposed to water, oxygen and nutrients. Vertical migration may only occur where channeling exists, and horizontal migration will occur at boundaries between fine grains and coarser-grained particles. Hydrocarbons would only slowly be washed out of the soil into the groundwater under these circumstances, and they would enter the groundwater in a relatively unaltered condition, even after many years of residence in the soil.

In contrast, highly aerated, wet and nutrient-rich environments in soil favors rapid degradation of a hydrocarbon fuel, which is the theoretical basis for bioremediation technology. The conditions in such soil promote very rapid changes in the composition of a fuel, which in some cases would result in almost complete hydrocarbon removal within a few months.

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Table 1
Biodegradation Ratios for Diesel Fuel No. 2

Sample	n-C_{17}/Pr	n-C_{18}/Ph	C_4-AB/C_2-Phen	C_1-Naph/C_2-Phen
Free floating product				
New diesel fuel	2.6	3.9	1.6	4.3
Degraded diesel fuel	1.2	1.4	1.2	3.4
Severly degraded diesel fuel	0	0	1.0	2.2
Soil Extract				
Degraded diesel fuel	1.1	0.8	1.7	3.2
Severely degraded diesel fuel	0	0	0.3	1.7

Table 2
Biodegradation Ratios for Bunker C Oil in Soil Extract

Sample	n-C_{17}/Pr	n-C_{18}/Ph	C_2-DBT/C_2-Phen	Chr/Phen	Phen:9+1/3+2
New Bunker C fuel	2.2	2.6	0.4	0.2	0.5
Degraded Bunker C fuel	1.6	2.0	1.3	0.3	1.1
Severely degraded Bunker C fuel	0	0	1.9	0.5	2.5

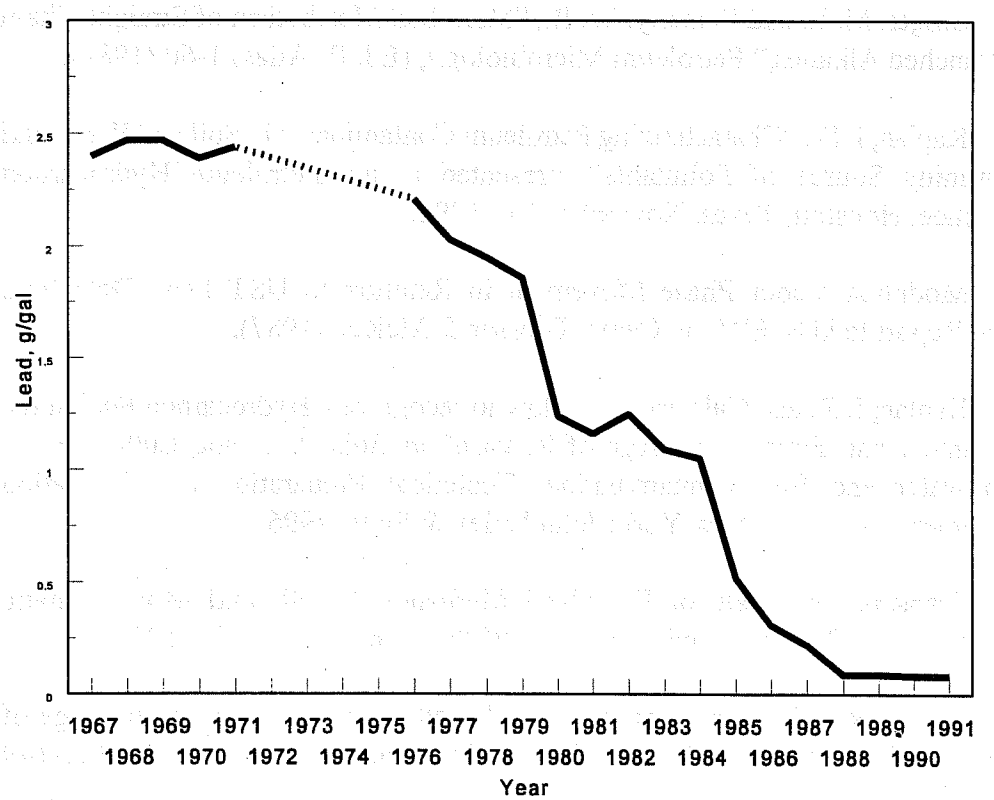


Figure 1. Historical trend in lead usage.

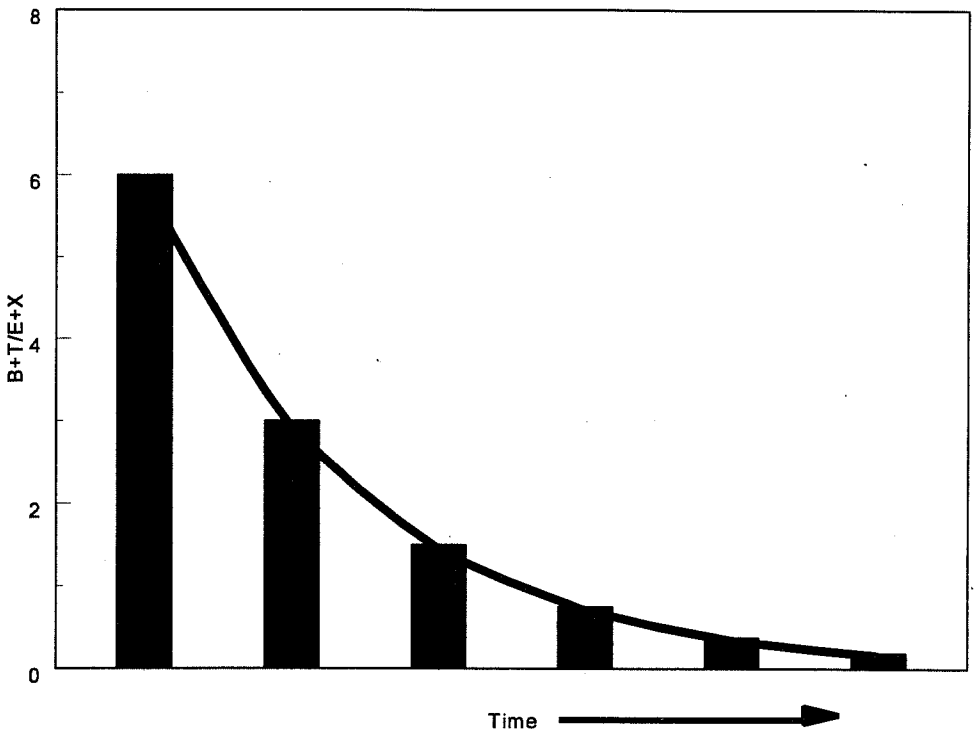
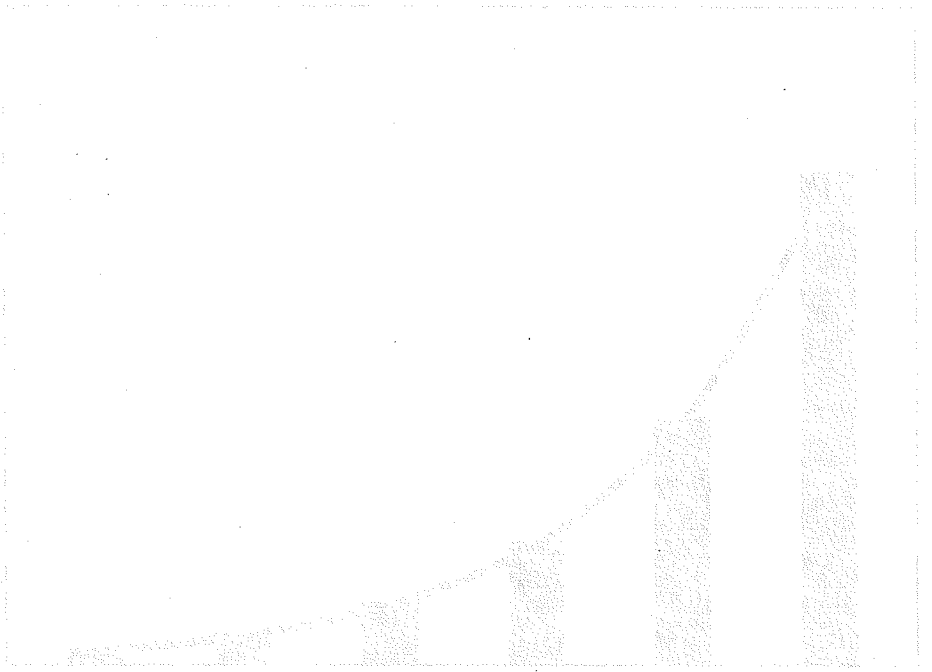


Figure 2. Time derivation based on decrease of B+T/E+X ratio with a half-life of five years.

Fuel Type	Level of Biodegradation	Chemical Compostion	Increasing level of biodegradation
Gasoline	1	Abundant n-alkanes	
	2	Light end n-alkanes removed	
	3	Middle range n-alkanes, olefins, benzene & toluene removed	
	4	More than 90% of n-alkanes removed	
Diesel	5	Alkylcyclohexanes & alkylbenzenes removed Isoprenoids & C_0-naphthalene reduced	
	6	Isoprenoids, C_1-naphthalenes, benzothiophene & alkylbenzothiophenes removed C_2-naphthalenes selectively reduced	
	7	Phenanthrenes, dibenzothiophenes and other polynuclear aromatic hydrocarbons reduced	
Bunker C fuel	8	Tricyclic terpanes enriched Regular steranes selectively removed C_{31} to C_{35}-homohopanes reduced	
	9	Tricyclic terpanes, diasteranes & aromatic steranes abundant	
	10	Aromatic steranes & demethylated hopanes* predominant	

* = Present under certain conditions only

Figure 3. Change in gasoline, diesel fuel and Bunker C oil compositions during biodegradation.



Anaerobic Biodegradation of Benzene and Toluene in Groundwater and Soil Samples

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Soil samples comprised of pulverized volcanic rock that was contaminated with both diesel fuel and gasoline were tested for the presence of organisms that can degrade toluene. Samples that were taken from four different depths from the two contamination sites were enriched under nitrate and sulfate reducing conditions for toluene degraders. All soil samples harbored both denitrifying and sulfate reducing populations as measured by activity assays. Initial toluene degradation rates under nitrate and sulfate reducing conditions were similar, $0.680 mg \cdot L^{-1} \cdot hr^{-1}$. Samples from pristine environments and samples from an aquifer contaminated with gasoline were also tested for the ability to biodegrade benzene anaerobically. Benzene biodegradation has not been observed in the pristine samples enriched for cultivation of methanogens, sulfate reducers and denitrifiers. Benzene biodegradation is apparent, however, in anaerobic enrichments of the contaminated aquifer sample. These enrichments have biodegraded benzene in the absence of an exogenous carbon source, and the activity occurred in the presence of 2mM sulfate or nitrate.

INTRODUCTION

The group of monoaromatic hydrocarbons known as BTEX (benzene, toluene, ethylbenzene, and the xylenes) and their presence in groundwater and soils is a widespread problem due primarily to the leakage of underground storage tanks at petroleum production wells, refineries, pipelines and distribution terminals (14). Guidelines have been established by the US Environmental Protection Agency for the cleanup of these chemicals in groundwater because of their carcinogenic potential (11). Although these aromatic hydrocarbons are relatively water soluble, they are in large part contained in the insoluble organic phase of the fuel which serves as a slow-release mechanism ensuring sustained, long-term contamination of groundwater sources (19).

Aerobic biorestoration has been shown to be effective for many fuel spills (34, for example). However, at contamination sites involving soils and groundwater, oxygen is the limiting factor for the degradation of these

components. Oxygen becomes limiting because of its rapid consumption, low solubility in water and low rate of transport through saturated porous matrices like soil and sediments. It is for these reasons that degradation of BTEX under anaerobic conditions by indigenous denitrifying (DNB) and sulfate reducing bacteria (SRB) would be a very beneficial process. Delivery of these electron acceptors to soil or aquifer organisms is facilitated by their high solubility. Another advantage is their low cost.

It has been widely reported that nitrate can serve as an electron acceptor during the anaerobic degradation of at least the TEX compounds (1, 9, 12, 14, 20, 40). Nitrate salts such as KNO_3 provide an ideal means to deliver highly soluble, energy efficient electron acceptor to indigenous bacteria capable of hydrocarbon degradation. Sulfate reducing bacteria have also been shown to degrade BTEX compounds under sulfate-reducing conditions (4, 23).

Complete mineralization of benzene under anaerobic conditions, however, has only recently been identified (10, 17, 23, 24, 35). While the TOL plasmid has been very well characterized, no enzyme system has been identified for the anaerobic biodegradation of benzene. This does not necessarily mean anaerobic benzene degradation is rare, however. It may just be mediated by extremely fastidious micro-organisms. Indeed, it has been estimated that less than ten percent of the micro-organisms in nature are cultivable. Nonetheless, reports of benzene biodegradation have demonstrated activity mediated by bacteria found in contaminated sites. Furthermore, SRB and methanogenic bacteria (MB) have been shown to be responsible for such activity (17, 23). Such evidence is lacking for DNB (26).

The history of anaerobic monoaromatic hydrocarbon degradation suggested that BTEX contaminated soils and groundwater might be examined for the presence of nitrate- and sulfate-reducing and methanogenic organisms capable of degrading BTEX compounds. In the study presented here, soil samples were assayed by the most probable numbers method and found to contain both DNB and SRB. Further enrichment of the soil samples under denitrifying and sulfate-reducing conditions showed that degradation rates under both conditions were similar on a biomass-protein basis. Enrichments for SRB and DNB found in BTEX contaminated groundwater demonstrated the ability to degrade benzene anaerobically. Slot blot analysis of soil and groundwater enrichment cultures revealed the presence of *xylE* (coding for catechol-2,3-dioxygenase, EC 1.13.11.2) but not *nirS* or *nirU* (coding for the heme and copper type nitrite reductases, respectively). In addition to soil DNA, soil 16S rRNA was probed with oligonucleotides specific to the genus *Desulfovibrio* and a broad group of sulfate reducers. Positive results were seen with both the *Desulfovibrio*-specific oligo probe and the probe specific for the group of sulfate-reducers in a subset of soil enrichments.

MATERIALS AND METHODS

Site History. Of the two soil plumes, one is contaminated with gasoline and the other with diesel fuel. The underlying soil is composed of volcanic rock and it is thought that there is little presence of other types of soils except for topsoil. In fact, soil samples obtained were primarily pulverized volcanic rock. All soil samples except the uncontaminated soil contained a great deal of organics as evidenced by their smell. The aquifer selected for study had been contaminated by an underground gasoline storage tank. Previous contamination of the aquifer dates back to the 1940s, and the leaky storage tank was removed in the mid-1970s. The groundwater still shows remarkable signs of contamination (see Table 1). Aquifer depth is around 6.4 meters.

Sample Designations. Soil samples: 10c, uncontaminated soil from a depth of 0-10ft; 27g, gasoline contaminated soil from a depth of 0-27ft.; 68g, gasoline contaminated soil from a depth of 60-80ft.; 10d, diesel fuel contaminated soil from a depth of 0-10ft. Groundwater samples: NB, groundwater enriched for denitrifiers, not amended with exogenous carbon-source; NT, groundwater enriched for denitrifiers, amended with toluene as an exogenous carbon-source; SB, groundwater enriched for sulfate reducers, not amended with exogenous carbon-source.

Soil MPN Analysis. Three-tube MPN trials were performed on all soil samples to obtain an estimation of the number of denitrifying and sulfate-reducing organisms present. 1/2 concentration nutrient broth (Difco) was amended with 5mM KNO_3 for denitrifying trials and Starkey's media (33) was modified by adding 5mM Na_2SO_4 and 31mM butyrate in addition to 31mM lactate for SRB. Denitrification activity was evidenced by gaseous nitrogen bubble formation in Durham tubes and sulfate-reduction activity was evidenced by the production of sulfide and the formation of a black precipitate (FeS). Extraction media for soils was 10% soil in Bushnell-Haas broth (DNB) and Starkey's media without lactate or butyrate (SRB). Both extraction media contained 0.1% Tween-80.

Toluene and benzene stocks. Toluene and benzene were prepared anoxically in appropriate media by adding toluene or benzene to their respective saturation points in water (515ppm for toluene and 1000ppm for benzene, 21).

Inocula and Enrichment Cultures–Soils. Triplicate samples were prepared for each soil under both denitrifying and sulfate-reducing conditions. For all samples, a basal salt medium, BSM 337 (27), was prepared and amended with 5mM sulfate or 5mM nitrate as appropriate. 14 ml of appropriate BSM 337 was

added to serum vials and loosely capped with crimp-top, Teflon-lined septa. Samples were then autoclaved. Upon removal from the autoclave, septa were crimped on tight and samples were flushed with nitrogen and evacuated to remove oxygen from the headspace. This process was repeated four times while media was still hot. Reducing agent (final concentration 248uM Na_2S and 496uM cysteine) was added to the sulfate-reducing vials and 1ppm Resazurin (redox indictor, 15) was added to both denitrifying and sulfate-reducing conditions. 300mg of each soil sample was then added to each vial under a sterile stream of nitrogen to keep oxygen from entering the vials.

Vials were inverted and incubated statically at room temperature overnight and the headspaces analyzed by GC for any volatile organic components. Toluene was then added to these samples at an initial concentration of 5ppm. Samples were analyzed by GC for toluene two hours later for a zero time and again at 24 hours. Eight days later, samples were spiked with 10 ppm toluene, analyzed two hours later and again 24 hours later. Toluene was then spiked in as needed when headspace analysis showed little or no detection of toluene by GC.

Sterile controls were also prepared by adding 300mg of each of the four soils to 14ml of BSM 337, autoclaving, waiting 24 hours and then autoclaving again. These samples were spiked with 10ppm toluene and analyzed concurrently with the active samples. Soil enrichments were transferred a total of four times from the original enrichments. These transfers were used for GC-MS, protein, DNA and rRNA analysis and were also always incubated statically at room temperature.

Groundwater samples. Triplicate samples were prepared for each sample of groundwater under denitrifying, sulfate reducing, and methanogenic conditions (Table 2). The denitrifying and sulfate reducing media contained a modified BSM337 containing 2mM nitrate and 2mM sulfate, respectively. The methanogenic media was prepared as previously descibed (2). A final volume of 60ml of each media was placed into 240ml amber bottles and fitted with Mini-Nert tops. Anoxic conditions were ensured as explained above. Reducing agent was added to the sulfate reducing and methanogenic media (0.5mM and 2mM Na_2S, respectively) and the vials were left static for 24 hours to guarantee anoxic conditions before inoculation. Vitamins, trace elements, and additional trace elements were added to the methanogenic media via sterile filtration before inoculation. Toluene was also added to appropriate bottles (Table 2) via sterile filtration. Finally, 60ml of groundwater was added to each bottle aseptically, leaving 50% headspace for GC analysis of benzene and toluene. Sterile controls were made by autoclaving (two times over a 48 hour period) one of the triplicates from each enrichment series.

After the 48 hour equilibration time, 2ppm benzene was added to each duplicate and sterile control (10ppm toluene was also added to the appropriate

microcosms). Vials were inverted and incubated statically at room temperature for 7 days before the headspaces were analyzed by GC for any volatile organic components.

Two independent transfers were made of the active cultures on days 44 and 164 by delivering 60ml and 20ml of the active culture, respectively, to fresh, sterile, anoxic media (as described above). The transfers were placed into 240ml serum vials fitted with crimp-on, Teflon-lined butyl rubber septa. The original cultures were replenished with fresh, sterile, anoxic media.

An additional 90ml was taken from each active culture during the second transfer, and the cells were harvested for nucleic acid extraction (by phenol extraction). The extracted DNA was used in the slot blot experiments.

Gas Chromatography and Mass Spectrometry. Headspace analysis on soil and aquifer enrichments was performed for toluene and benzene on an HP 5890 Series II gas chromatograph equipped with an HP-5 column and FID. Standard curves were produced with each analysis to quantitate toluene and benzene. Mass Spectrometry analysis was performed on soil enrichments on an HP 5890 GC equipped with an HP 5971A Mass Selective Detector. For mass spectrometry, cultures were acidified to pH 3.0, extracted with methylene chloride, reduced and resuspended in diazomethane for derivatization (methylation) of compounds with alcohol, aldehyde, and carboxylate moieties. Positive controls were benzoate and phenol extracted from media. Protein analysis for soil enrichments was performed by a modified Lowry method (25).

Slot Blot Hybridization. DNA of soil and aquifer enrichments was analyzed for the presence of the *xylE* (3) and *nirS* (32) genes by the slot blot method (Zeta-Probe, Bio-Rad). Six negative control DNA samples were used with genomic DNA probes: *Klebsiella pneumoniae, Enterobacter aerogenes, Proteus vulgaris, Rhizobium meliloti, Bacillus megaterium* and *Rhodococcus erythropolis*. 16S rRNA of soil enrichments (fourth transfer) cultured under anaerobic and aerobic conditions (100% O_2 headspace) were also targeted with oligonucleotide sequences specific for the *Desulfovibrio* genus (probe 687) and a large group of SRBs (probe 804) (8). *xylE* and *nirS* probes were synthesized with a Random Primer DNA Labeling Kit (Sigma) incorporating ^{32}P d-CTP. Oligonucleotide sequences were labeled with digoxigenin (DIG-ddUTP, anti-digoxigenin antibody conjugated to alkaline phosphatase). Negative controls were *E. coli* and calf RNA. Control DNA was pUC18 DNA and control oligonucleotide was DIG-ddUTP-labeled (Genius System, Boehringer-Mannheim).

RESULTS

Soil MPN Analysis. For the four soil samples tested under denitrifying conditions the results were as follows as interpreted by published three-tube MPN tables (Harrigan, 1970): 10c, $2.0 \cdot 10^7$, category 1; 27g, $1.5 \cdot 10^7$, category 2; 68g, $4.5 \cdot 10^7$ category 1; 10d, $2.0 \cdot 10^7$, category 3. Results for sulfate reducer MPNs yielded combinations (category 3 & 4) that are statistically highly unlikely (38) and could not be used as a basis for evaluation. However, positive results were seen for all soil samples under sulfate-reducing conditions.

Gas Chromatography-Protein Analysis. Degradation rates based on GC data as well as concurrent protein analysis provided very similar rates of toluene degradation in the four soil enrichments. In DNB enrichments, toluene degradation rates averaged $0.680 mg \cdot L^{-1} \cdot hr^{-1}$ and specific activity was calculated to be 0.063mg toluene$\cdot hr^{-1} \cdot$mg protein^{-1} with all four soil samples being averaged. In SRB enrichments, rates were also similar ($0.680 mg \cdot L^{-1} \cdot hr^{-1}$) to the rates for DNB enrichments. Average specific activity for SRB was 0.315mg toluene$\cdot hr^{-1} \cdot$mg protein^{-1}. Figures 1 and 2 show the initial soil enrichments and toluene degradation activity under denitrifying and sulfate-reducing conditions. These early enrichments exhibited lower degradation rates then those determined in later transfers.

Degradation of benzene also occurred in two aquifer enrichments in the absence of exogenous carbon-source (both NB and SB, Figures 3 & 5) and in the presence of exogenous toluene (NT) (Figure 4). In addition, degradation continued concurrently with toluene degradation each time fresh toluene (10ppm) was delivered to the active cultures (days 1, 8, 20, 172, 218; data not shown). Degradation also continued in the original microcosms after each transfer (days 44 and 164), and it continues today in all of the originally active cultures, except for SB1.

Transfers of the active cultures to fresh media have not shown activity, and delivery of 0.5mM Na_2S to the original SB series has inhibited benzene degradation (Figure 5).

Slot Blot Hybridization. Strong hybridization of all four soil sample enrichments was seen with the use of *xylE* in an initial probe with all four soil enrichments under both denitrifying and sulfate-reducing conditions, but hybridization with the *nirS* gene appeared to be weak (Figure 6). Denitrifying groundwater enrichments also hybridized strongly with the *xylE* probe in the same procedure. A second, higher stringency washing (70°C) failed to remove faint bands from the blot (data not shown). These results were repeated in a second probing of aerobic and anaerobic treatments of sample 27g of the fourth soil enrichment transfer (Figure 6). Three of six negative controls hybridized with the *xylE* probe and two of the six negative controls hybridized with the *nirS* probe,

though *R. meliloti* has been shown to denitrify and so probably harbors an *nir* gene (39).

16S rRNA probes also yielded positive results using both the *Desulfovibrio* genus and broad group SRB probes in both anaerobic and aerobic treatments of sulfate-reducing enrichments of transfer four though signals were weak (data not shown). Suprisingly, bands for the sulfate-reducing enrichments grown under aerobic conditions were approximately five times stronger than those of the anaerobic treatment. Hybridization to both probes also occurred with a denitrifying enrichment grown under aerobic conditions. Negative control RNA (*E. coli* and bovine calf) showed no hybridization with either probe.

DISCUSSION

Soil Samples. Soil MPN analysis revealed that both denitrifying and sulfate-reducing bacteria were present in all soil samples. Good statistical data was obtained for denitrifier MPNs but it is believed that the best information provided by the results of the sulfate-reducer MPNs is that sulfate reducing bacteria are present in all of the soil samples, many of which belong to the genus *Desulfovibrio* as evidenced by the oligonucleotide probe. Comparable rates of degradation were seen in all soil samples. Under aerobic conditions, rates of degradation were consistent with those of anaerobic treatments. Based on protein production, comparable rates of degradation were again seen. Degradation was seen to occur in redox conditions from +321 to -51mV. However, all transfers of soils enrichments were found to degrade only a fixed amount of toluene (ca. 60-75μmol) before activity stopped. The amount of oxygen present in the media of new transfers (assuming a total nitrogen headspace) should only be in the range of 8-9mg/L (5). By looking at mass balance equations for the degradation of toluene under energetically favorable aerobic conditions, it can be seen that this is only enough oxygen to completely oxidize approximately 5.5μmol of toluene (30).

Therefore, it may be hypothesized that aerobic, TOL plasmid (containing *xylE*) positive organisms (possibly facultative oxygen/nitrate respiring) capable of degrading toluene exist in the enrichments and may, at first, be oxidizing toluene aerobically and supplying anaerobes with intermediates (assuming no degradation of their own) who maintain an existence with these intermediates. This hypothesis is supported by the probe results with *xylE* seen in figure 5. Even under low redox conditions, aerobic activation of toluene may be occurring, thus causing the further disappearance but not complete degradation of toluene. At the point where toluene degradation ceases, nitrate is still present (as spot-checked with dimethylamine) as is sulfate (total sulfate assay). In fact, sulfate concentrations were not seen to decrease over the course of experimentation in at least one of the enrichment transfers. Mass spectrometry analysis yielded no derivatized intermediates of any known toluene degradation pathway.

Enrichments must be analyzed further under long-term conditions to see if activity resumes after redox conditions have become more reducing.

It is possible that metabolites from aerobic organisms may be supporting anaerobic organisms in soil enrichments, where anaerobic organisms might be found in the anoxic zones of vials that were incubated statically. It is not known why hybridization occurred with the *Desulfovibrio* and SRB group probes in the denitrifying enrichments grown under anaerobic conditions, however, it is known that nitrate reduction can occur in SRB like *Desulfovibrio desulfuricans* (7, 31). It is also known that dissimilatory sulfate-reducing bacteria can use compounds like fumarate and malate (28, 29), as well as CO_2 (22), as electron acceptors. With a much larger supply of oxygen (as in the aerobic treatments), it may be hypothesized that toluene degradation would occur more by aerobic, energetically favorable reactions. This metabolism may create more carbon intermediates (that would serve as both electron donors and electron acceptors) that could support an anaerobic population in the cultures.

The indication of the presence of the *xylE* gene is encouraging as it provides evidence of the presence of the TOL plasmid (*meta*-cleavage pathway) in both the soil and aquifer samples. Conclusions from probe results must be tempered by the hybridization of *xylE* probe with three of the six negative control DNA. One explanation of those unexpected results is that perhaps these organisms contain a catechol-2,3-dioxygenase (C23O) enzyme that is normally not found in nature in TOL plasmid negative organisms. There is currently no broad base of reference for which specific organisms contain C23O (EC 1.13.11.2), C12O (catechol-1,2-dioxygenase, EC 1.13.11.1) or both, as was found in *Pseudomonas putida* mt-2 (13). Also, information is scarce as to whether C230 may exist without the entire compliment of TOL plasmid genes. To date, there has been relatively little work done on the distribution and characterization of these enzymes and their isozymes in nature.

Aquifer Samples. Gas chromatography analysis of benzene levels in the aquifer enrichments reveals that both SRB and DNB degraded benzene in the absence of exogenous carbon-source, as well as in the presence of exogenous toluene (DNB only). No lag time is reflected by the data, and the initial levels of benzene on day zero demonstrate how quickly benzene was degraded once introduced. Since the microcosms were left to equilibrate for 7 days before initial analysis, the first incidence of benzene degradation was not identified. In addition, the perturbation caused by the removal of 50% of the culture during the first transfer, and removal of >90% of the culture during the second transfer and cell harvest caused no apparent loss of activity.

Benzene degradation from day 218 onward has been variable. Of the six live samples, only the SB1 replicate has stopped (NB1, NB2, NT1, NT2 and SB2 continue degrading benzene). Loss of degradation activity in SB1 is not surprising

considering these cultures are more than one-year old. However, efforts to transfer the activity into fresh media have failed. The degradation activity we have observed must be anaerobic because mass balance equations similar to those calculated for toluene above indicate that 8μmol of benzene would consume the oxygen found in saturated media, again assuming a completely anoxic headspace. In this experiment, more than 100μmol benzene has been consumed by the active cultures. This is well in excess of the calculated theoretical amount of benzene that could be oxidized aerobically.

The hybridization of *xylE* to DNA extracted from NB and NT indicates that benzene degradation may have occurred in these samples via TOL plasmid expression. It is uncertain, however, since the *xylE* probe hybridized to three of the six negative controls. Though these bacteria used as controls may have homologous sequences, we plan on sequencing the *xylE* probe to verify its TOL plasmid origin.

These studies provide a quantitative description, through basic enrichment techniques, contaminant addition to enrichments, and genetic analysis of the microflora that is found in these soil plumes and groundwater samples. Results in these experiments are encouraging and provide an overall idea as to how to set up a second phase study using soil core columns to test the effect of electron acceptors, such as nitrate, sulfate, to stimulate the biological removal of organic contaminants found in the plumes.

Table 1.
Approximate concentrations of indigenous BTEX detected in groundwater effluent (ppm). ND: not detected. Averages calculated from Cadena, et al., NM WERC, Project Number: 01-4-23296.

Benzene	Toluene	Ethyl-benzene	m-,p-xylenes	o-xylene
1.13	0.05	1.97	3.35	ND

Table 2.
Aquifer samples were enriched for denitrifying, sulfate reducing, and methanogenic micro-organisms. Within each group, triplicate-sample series were ammended with an exogenous carbon-source, or with no exogenous carbon-source (benzene only).

Enrichment	Series	C-source Ammendment	Benzene/Toluene Degradation?
Denitrifiers	NB	Benzene only (2 ppm)	Yes
	NT	Benzene, toluene (2, 10 ppm)	Yes (Benzene & toluene)
	NBT	Benzoate (1 mM)	No
Sulfate Reducers	SB	Benzene only (2 ppm)	Yes
	SE	Lactate/pyruvate/glucose (5 mM each)	No
Methanogens	MB	Benzene only (2 ppm)	No
	MM	Methanol/Acetate (10 mM each)	No
	MG	Glucose (10 mM)	No

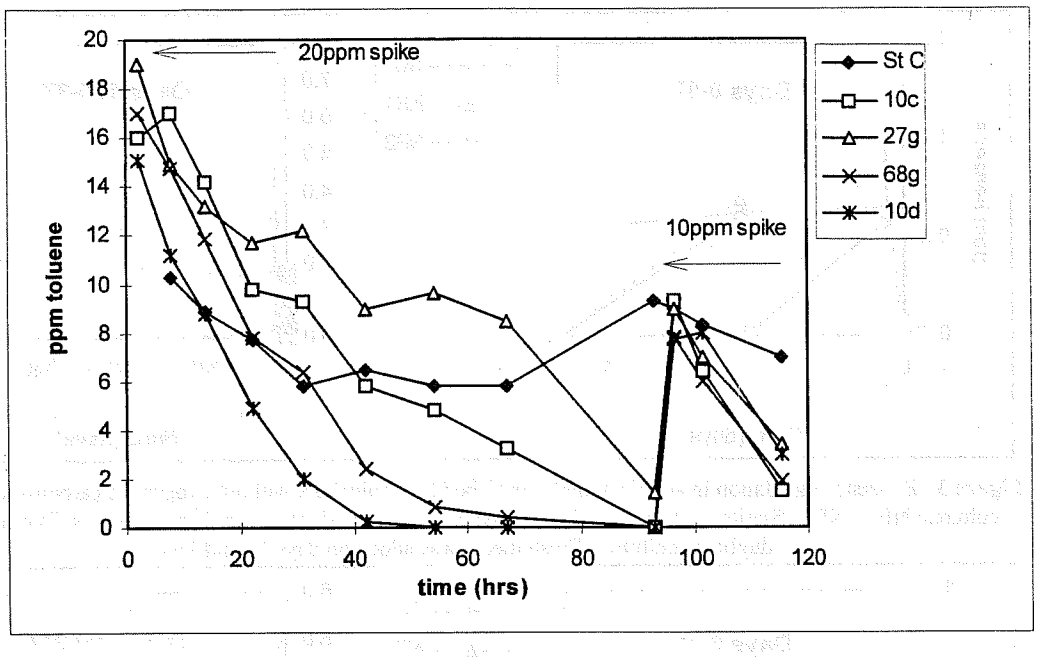

Figure 1. GC analysis of toluene in initial soil enrichments under denitrifying conditions. Samples are in triplicate and are discussed in Materials and Methods section. Data shown is a time-period after initial 5 and 10 ppm toluene amendments. St C, sterile controls in quadruplicate.

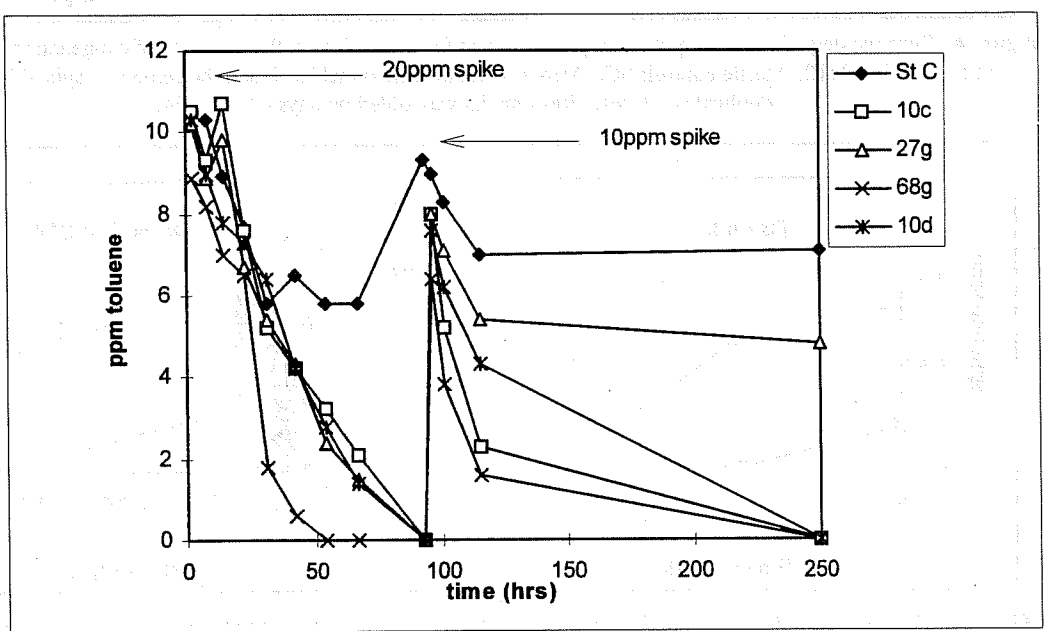

Figure 2. GC analysis of toluene in initial soil enrichments under sulfate-reducing conditions. Samples are in triplicate and are discussed in Materials and Methods section. Data shown is a time-period after initial 5 and 10 ppm toluene amendments. St C, sterile controls in quadruplicate.

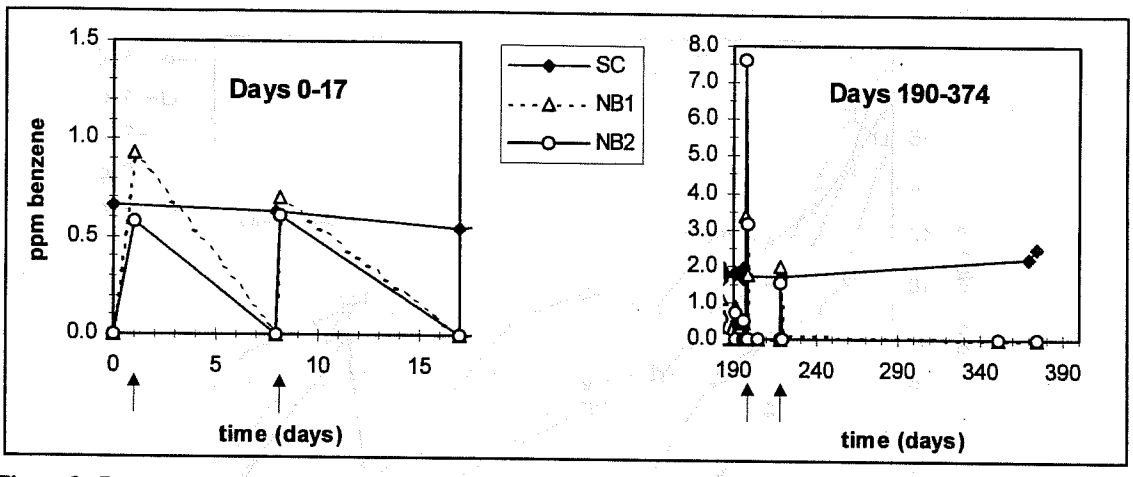

Figure 3. Benzene degradation in aquifer samples enriched for denitrifiers without exogenous carbon-source. Live cultures: NB1 , NB2. Sterile control: SC. Arrows indicate days on which 2 ppm benzene was spiked into both duplicate cultures. Fresh media was added on days 44 and 164.

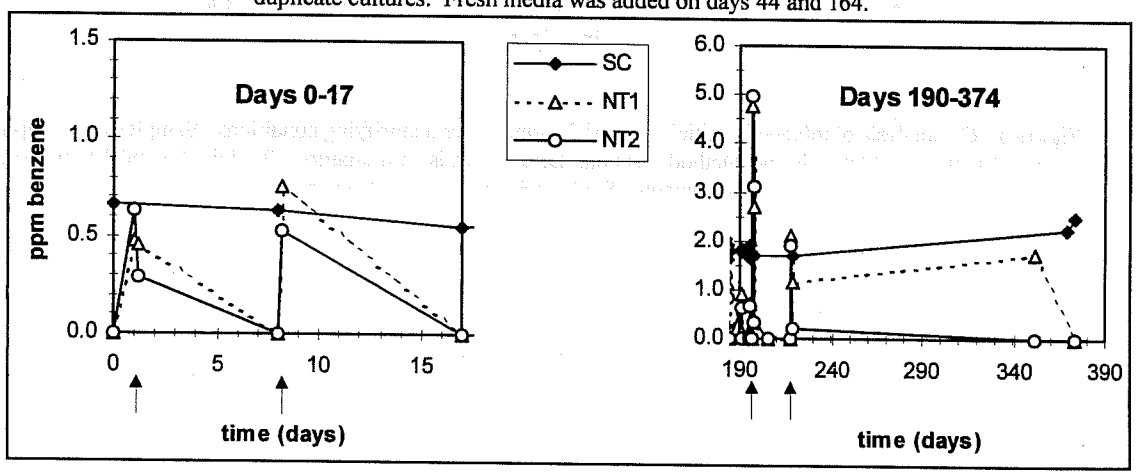

Figure 4. Benzene degradation in aquifer samples enriched for denitrifiers in the presence of exogenous toluene. Live cultures: NT1 , NT2. Sterile control: SC. Arrows indicate days on which 2 ppm benzene was spiked into both duplicate cultures. Fresh media was added on days 44 and 164.

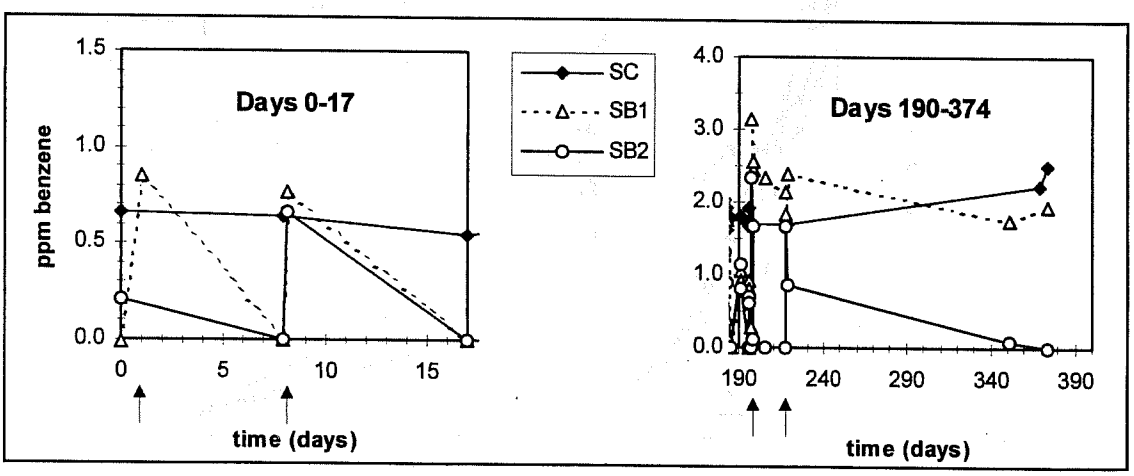

Figure 5. Benzene degradation in aquifer samples enriched for sulfate reducers in the absence of exogenous carbon-source. Live cultures: SB1 , SB2. Sterile control: SC. Arrows indicate days on which 2 ppm benzene was spiked into both duplicate cultures. Fresh media was added on days 44 and 164. Additional Na_2S (0.5mM final concentration) was added on day 191.

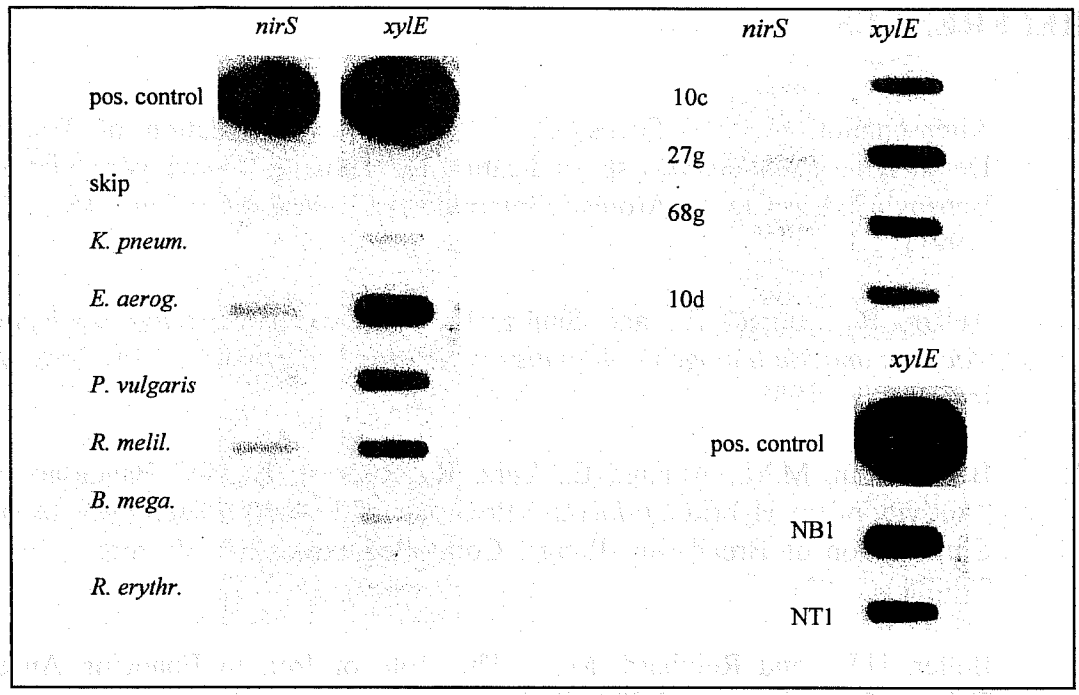

Figure 6. Slot blots of soil enrichment transfers. *nirS,* nitrite reductase (heme type); *xylE,* catechol-2,3 dioxygenase. See Materials and Methods for soil and aquifer sample designations. Lower right blot is from the initial probe with *xylE.* Left and top left blots were from second probing. Postive controls were plasmid DNA harboring *nirS* and *xylE.*

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Nitrogen Cycling in Oil-Impacted Soils

I. Microbial Effects

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Abstract:

A site in the Tallgrass Prairie Preserve (The Nature Conservancy, Pawhuska, OK), accidently contaminated with crude oil from a pipeline break, was treated by tilling the contaminated soil together with uncontaminated soil, hay, phosphate and potassium. The site was divided into four contiguous plots and treated with defined oxidized and reduced nitrogen fertilizer. One plot (Control) received no added nitrogen, another received urea, a third ammonium sulfate, and the fourth ammonium nitrate. The plots were monitored approximately three months for the following: the level of ammonium, nitrite, and nitrate in the soil, nitrifying and denitrifying bacteria, production of gases known to affect ozone levels (NO_2 and NO), and other soil gases indicative of microbial respiration (O_2, CO_2).

Respiration levels were found to vary over time in the bioremediated area, but were higher than in the surrounding uncontaminated prairie soil. Ammonium levels remained elevated throughout the duration of the study in treatments in which ammonium had been added, while nitrite increased to very high levels in the urea treatment. Urea-treated soil had the highest level of NO flux. Ammonium oxidizers were very abundant on all sample dates. Nitrate-reducing and denitrifying bacteria soon became very abundant in the nitrogen-treated plots. Nitrite oxidizers were below the level of detection except on one sample date. Nitrite levels decreased between two sample dates only in treatments with detectable numbers of nitrite oxidizing bacteria.

Introduction:

Stimulation of bioremediation by fertilization

The goal in bioremediation of petroleum-contaminated sites is to stimulate the activity of petroleum hydrocarbon-degrading bacteria in order to prevent damage from spreading and to restore the contaminated sites. The addition of nitrogeneous fertilizer is often recommended to enhance bioremediation by supplying nutrients such as nitrogen or phosphate that may be limiting microbial activity and hence biodegradation (1). However, depending upon the chemical composition of the fertilizer and other chemical and physical conditions at the site, fertilization may promote the growth of certain groups of microbes over that of others by supplying compounds such as NO_3^- that can be used as electron acceptors by nitrate reducing and denitrifying bacteria; or, in the case of ammonium, as an electron donor by nitrifying bacteria, specifically the ammonium oxidizers. Stimulation of denitrification and/or nitrification can increase the emission of microbially produced gaseous nitrogen oxides (2), and thus bioremediation may have unanticipated effects on the production of these gases.

Microbial production of gaseous nitrogen oxides and regional ozone levels

In rural areas, ozone levels have been found to be strongly associated with the level of gaseous nitrogen oxides (N_2O, NO, and NO_2, 3). Soil microbes have been implicated in the production of these gases since measurements indicate that soil is a significant source of nitrogen oxides, and in most soils, is primarily microbial in origin (2).

NO and N_2O are produced by denitrifying bacteria during dissimulative reduction of nitrate to N_2 (2). The ability to perform dissimulative nitrate reduction is fairly widespread among bacteria, including members of such common soil genera as *Pseudomonas* and *Alcaligenes* (4). These bacteria are heterotrophic facultative anaerobes; denitrification is surpressed in the presence of sufficient oxygen, which is energetically a more favorable electron acceptor than is nitrate (4). Although the control of denitrification is complex and not completely understood, denitrification is known to increase when simultaneously the levels of carbon and nitrate are high, and oxygen tension is low (2).

Nitrification is performed sequentially in two phases, e.g., ammonium oxidation and nitrite oxidation, by different groups of autotrophic chemolithotrophs (*4*). NO and N_2O are thought to be produced by reduction of nitrite by ammonium oxidizers under certain conditions, although the exact mechanism is still under examination (2). The level of nitrification, the production of NO and N_2O, and the NO/N_2O ratio, are known to be influenced by the availability of ammonium and oxygen, as well as by other factors such as temperature and water potential (2). Although both groups of microbes are commonly found in most soils, the nitrite oxidizers in

particular are very sensitive to environmental stress, and their absence or diminished activity may lead to a build-up of nitrite under certain circumstances (2).

The objective of the study reported here is to determine the effect of bioremediation of crude oil-contaminated soil on nitrogen oxide emissions from soil; specifically, to compare the effect of adding various nitrogenous fertilizers on: 1) microbial respiration, 2) soil chemical parameters important for microbial activity, and 3) the number of nitrifying and denitrifying bacteria.

Materials and Methods

Site history

The study site is located within the bison grazing range in the Tallgrass Prairie Preserve (Pawhuska, OK; The Nature Conservancy). This region in northern Oklahoma and southern Kansas has historically been the locale of oil production. In 1992 an accidental pipeline break contaminated an area approximately 14 yards (at widest) by 38 yards with crude oil. Contamination levels ranged from 6,000 to 33,000 mg/kg, when tested in 1995 (3 samples, Total petroleum hydrocarbons by EPA Method 418.1, Southwest Laboratory of Oklahoma, Inc.)

Treatments

Bioremediation of the site began in May 1996. The contaminated soil was mechanically moved to a treatment site adjacent to the west and mixed with uncontaminated soil (free of petroleum and brine) at a 5:1 ratio, bringing the level of total petroleum hydrocarbons (TPH) to less than 3%. The amount of N, P, and K added were chosen to give the ratio of 100 C:10 N: 1 P, K , recommended for effective bioremediation of petroleum hydrocarbons by landfarming (1), but with 1/3 of the final amount of N applied initially. Three hundred fifty lbs P_2O_5, 250 lbs K_2O, 75 bales of prarie hay and 42 bags of bison manure were applied evenly across the treatment site. The treatment site was then divided into four contiguous strips with nitrogenous fertilizer applied evenly to the individual treatment strips as follows: Control (C), no nitrogen fertilizer added; Urea (U); Ammonium sulfate (S); and Ammonium nitrate (N) to give on the average 1000 ppm (w/w) nitrogen. All the above additions to the treatment site were mechanically tilled to mix, resulting in an irregular quadrangle (79-94 ft. by 90 ft.) of treated soil approximately 12 inches deep resting on uncontaminated soil.

Soil sampling and compositing

The outside vertices of each of the four treatment sites were marked with wooden stakes, and five wooden stakes were also permanently installed in each of the four sites to serve as ordination points for soil

sampling. The pattern of placement of the ordination stakes formed a flattened "W" , with each stake being three feet from the edge of the treatment strip. Soil gas surveys and collection of soil for chemical analysis and for bacterial enumeration (see below) were made at the same defined distances and orientation from the ordination stakes during any one collection date. The survey and collection sites were at a different distance and orientation for each different collection date (May 21, May 29, June 5, June 12, July 1, and August 1) so the same soil was not resampled. Surveys and collections were made at two different depths ("Levels") in the soil: Level 1 was 1-6" below the soil surface, Level 2 was 7-12" below the soil surface. Soil from the same level and treatment was composited (see below), giving a total of eight composited samples. Soil was also collected from the prairie ("Pr") several hundred yards to the west of the treatment area to serve as an uncontaminated control.

Soil gas survey

Soil gases (O_2, CO_2) were monitored on each collection date using a GasTech O_2/CO_2 Monitor with an internal vacuum pump. Atmospheric standards of O_2 at 20.9% and CO_2 at 0.05% were used to calibrate the monitor. Level 1 gases were sampled 4-6" below the surface, level 2 at 7-11" below the surface.

Chemical analyses

Soil samples for analysis of cations and anions (NO_2^-, NO_3^-, Cl^-, Na+, Ca^{2+}, Mg^{2+}, K^+, HPO_4^{2-}, SO_4^{2-}) were prepared by grinding, then mixing with water by vortexing. After centrifugation the supernatant was applied to the autosampling vial of a Dionex DX-100 Ion Chromatograph with an Ion 4G Column. pH was determined after water extraction, % moisture was determined by gravimetric measurement after oven drying. Cation Exchange Capacity (CEC) was determined using standard techniques (5). Ammonia/ammonium was determined by a colorimetric technique using Nessler's Reagent following extraction with 1M NaCl (5).

Enumeration of denitrifying and nitrifying bacteria

Sterile isotonic saline (25 mL, 0.85% NaCl, pH 7.0) containing 100 ug/mL cycloheximide (a fungicide) was added to composited soil samples (1/2 g from each of 5 collection sites/treatment level, or 2.5 g total for each treatment-level), vortexed, serially diluted in sterile saline containing 100 ug/mL cycloheximide, and used to inoculate (1/10 dilution) microtiter plate wells containing nitrate broth (for enumerating nitrate reducers and denitrifiers), ammonium mineral salts medium (ammonium oxidizers), or nitrite mineral salts medium (nitrite oxidizers)(6). Three rows of wells/type of media were inoculated to give a three-tube MPN. The microtiter plates were incubated in the dark at room temperature for the following periods then examined for conversion of the initial nitrogenous compound using standard colorimetric tests for the detection of nitrite (6): 14 days (nitrate

reducers and denitrifiers), or 42 days (ammonium- and nitrite oxidizers). The number of bacteria in each of the catagories was estimated from standard MPN tables using the distribution of wells showing the appropriate color reaction. A row of wells in each plate was filled with media and incubated for the appropriate length of time, but not inoculated, served as a sterile control.

Results and Discussion

Soil gases

The rate of microbial respiration (Figure 1) appeared to be higher in the bioremediated area: oxygen levels in the treatment area were generally lower, and CO_2 levels higher, than either atmospheric standards or uncontaminated prairie soil (surveyed May 29, July 1). Based on the degree of depression in O_2 and rise in CO_2 it appeared that June 12 marked the peak of microbial activity. Heterogeneity was striking: measurements varied among sites within treatments as much as the treatments varied among themselves, with the possible exception of August 1. It was not always possible to obtain five Level 2 measurements from each treatment because compaction of the soil prevented adequate flow to the monitoring instrument.

Chemical analyses

The % moisture, Cl^-, Na^+, CEC, and HPO_4^{2-} levels were similiar among all treatment levels, and higher than the uncontaminated prairie (Table 1). The S treatment (ammonium sulfate) had, as expected, a much higher level of SO_4^{2-}, as well as higher Ca^{2+} and Mg^{2+}. The initial pH values in U (urea) were higher than in C (control), and those in S and N (ammonium nitrate) were lower than in C. Final pH values were between 6 and 8 for all treatments. Each treatment had a unique combination of N ion levels (Figure 2): C and Pr (prairie) remained low for all three, U had high levels of ammonium, especially in the upper level and attained moderate levels of nitrate, S and N both had moderate levels of ammonium and low levels of nitrite, but the level of nitrate rose over time in S, while it decreased in N. The most striking feature was the build-up of high levels of nitrite in U.

Bacterial enumeration

The estimated number of denitrifying bacteria in the U, S, and N treatments quickly rose more than 10-fold, in some cases 1000-fold, during the 3 month sampling period (Figure 3, top). C and Pr showed a different pattern: moderate levels until after July 1, then a rise to extremely high numbers on August 1. The number of ammonium oxidizing bacteria was always greater than could be estimated using this dilution series (upper

limit of detection: 10^{10}/g soil). Nitrite oxidizers were not detected (detection limits: $<10^{3}$/g soil) except from the July 1 sample.

Nitrite levels, nitrite oxidizers, and NO

The number of nitrite oxidizers on July 1 was associated with change in the level of nitrite from the previous (June 12) sampling date: treatments with more nitrite oxidizers had greater decreases in the level of nitrite, while U, with no detected nitrite oxidizers, had a sustained increase in the level of nitrite (Figure 3, bottom). U also had by far the highest level of NO flux, as measured with a chemiluminescent analyzer (7).

SUMMARY

Microbial respiration

Respiration levels varied over time in the bioremediated area, but were higher than in the surrounding uncontaminated prairie soil.

Soil Chemistry

Ammonium levels remained elevated throughout the duration of the study in treatments in which ammonium had been added (U, S, N).

Nitrate levels dropped from high initial values in N and rose in S and U over the course of the study.

Nitrite increased to very high levels in U.

Initial pH values were higher than C in the U treatment, and lower in S and N treatments. Final values for all were between pH 6 and 8.

Bacteria

Ammonium oxidizers were very abundant on all sample dates. Nitrite oxidizers were below the level of detection except on one sample date. Nitrate-reducing and denitrifying bacteria soon became very abundant in the nitrogen-treated plots (U, S, N), and later in the C and Pr areas.

Nitrite levels and nitrite oxidizing bacteria

Nitrite levels decreased between two sample dates only in treatments with detectable numbers of nitrite oxidizing bacteria.

CONCLUSIONS

Fertilization of petroleum-contaminated soil may have the secondary effect of stimulating the processes of denitrification and nitrification. Certain fertilizers, such as urea, may contribute to conditions that uncouple the two phases of nitrification (ammonium oxidation and nitrite oxidation), allowing higher production of NO. In support of this hypothesis, it was found that 1) soil treated with urea built up high levels of nitrite, 2) no nitrite

oxidizing bacteria were detected in the urea-treated soil, and 3) urea-treated soil had high rates of NO flux.

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Table 1

Soil Chemistry: Range of Values Over Sampling Period*

Treatment	Level	pH**	% H_2O	Soluble Cations and Anions (ppm)					CEC	HPO_4^{2-***}	SO_4^{2-***}
				Cl^{-***}	Na^{+***}	Ca^{2+***}	Mg^{2+***}	K^{+***}	(meg/100g)	(ppm)	(ppm)
C	1	6.9 - 7.8	13 - 19	185 - 229	32 - 50	175 - 200	27 - 40	47 - 73	11.04 - 18.52	0 - 20	40 - 116
	2	6.8 - 8.0	15 - 19	70 - 225	53 - 92	129 - 180	16 - 41	22 - 50	9.83 - 17.74	0 - 46	50 - 128
U	1	7.8 - 8.6	14 - 17	220 - 473	30 - 33	79 - 151	29 - 80	30 - 289	11.57 - 20.70	0 - 40	44 - 154
	2	7.3 - 8.8	16 - 21	30 - 380	54 - 79	143 - 151	28 - 39	50 - 93	12.17 - 20.17	0 - 59	35 - 144
S	1	6.2 - 6.9	14 - 17	144 - 398	29 - 42	353 - 1003	93 - 177	42 - 132	16.78 - 17.48	0 - 79	2010 - 4350
	2	6.3 - 7.4	16 - 21	88 - 291	23 - 51	233 - 976	60 - 99	48 - 88	12.96 - 15.30	0 - 14	582 - 5360
N	1	5.6 - 6.4	14 - 17	144 - 300	23 - 35	280 - 490	68 - 113	26 - 198	17.04 - 20.43	0 - 38	11 - 222
	2	5.8 - 6.8	17 - 22	57 - 387	23 - 78	230 - 322	51 - 65	28 - 74	17.48 - 20.43	0 - 117	4 - 349
Pr	1	n/a	7 - 18	3	n/a	n/a	n/a	n/a	n/a	0	10
	2	n/a	n/a	1	n/a	n/a	n/a	n/a	n/a	0	0

* Sampling Dates: 5/21, 5/29, **6/5**, **6/12**, **7/1**, 8/1 (bold dates for Mg^{2+}, Ca^{2+}, CEC). n/a: not available

** Water Extracted

*** Sample was prepared by grinding, then mixed with water and centrifuged.
Supernatant was applied to the autosampling vial of a Dionex DX-100 Ion Chromatograph with an Ion 4G column.

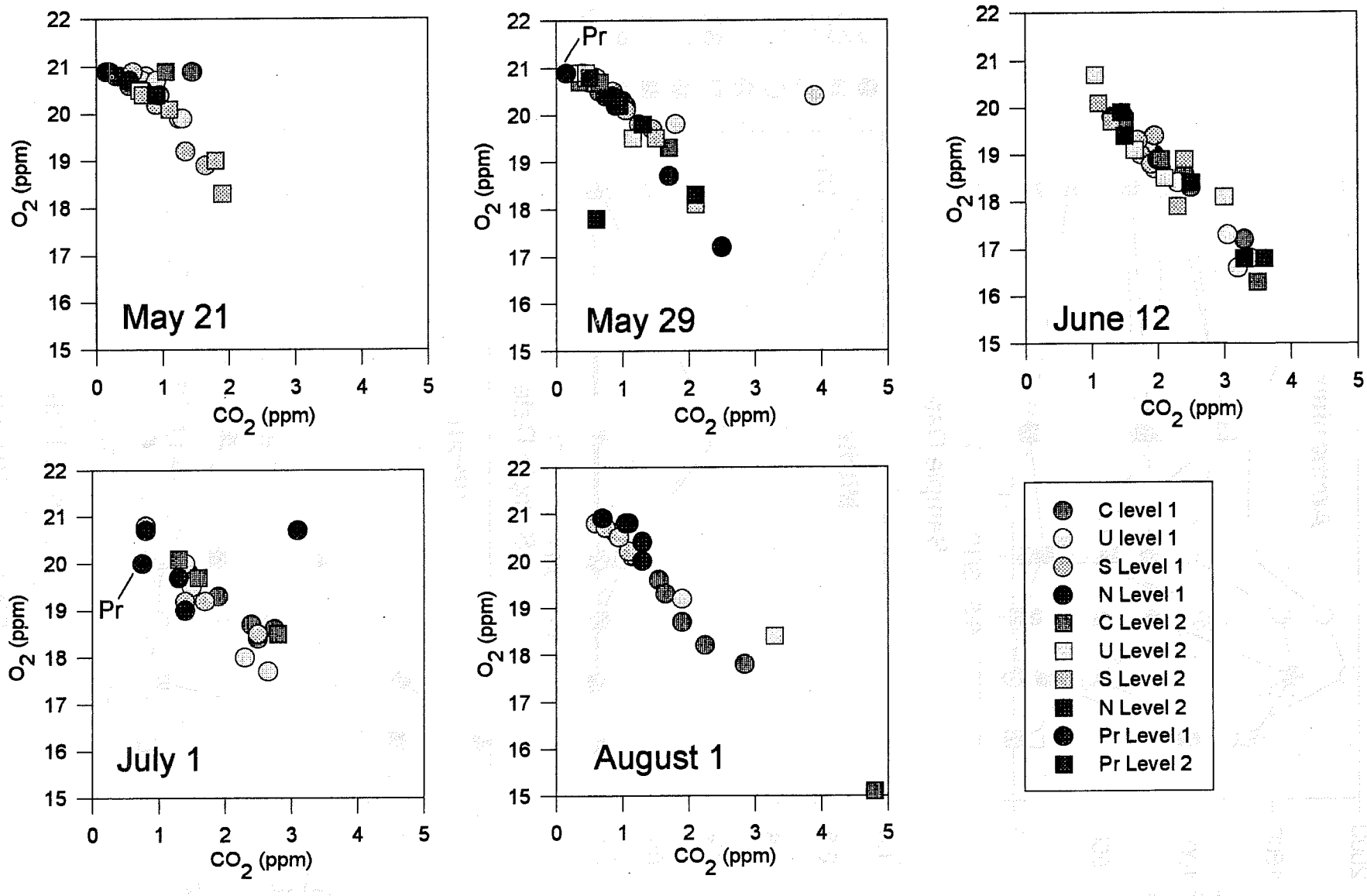


Figure 1. Soil Gas Measurements

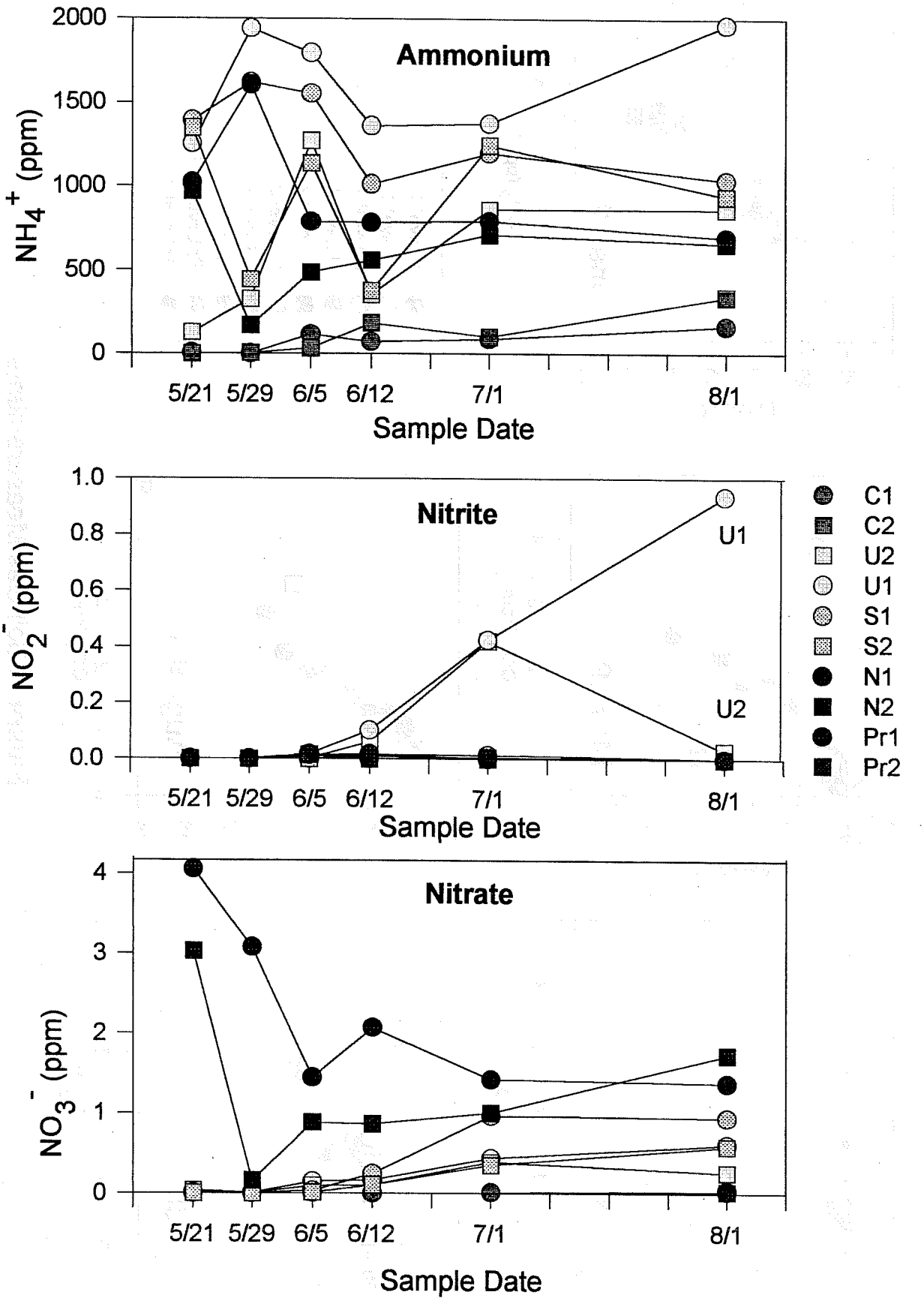
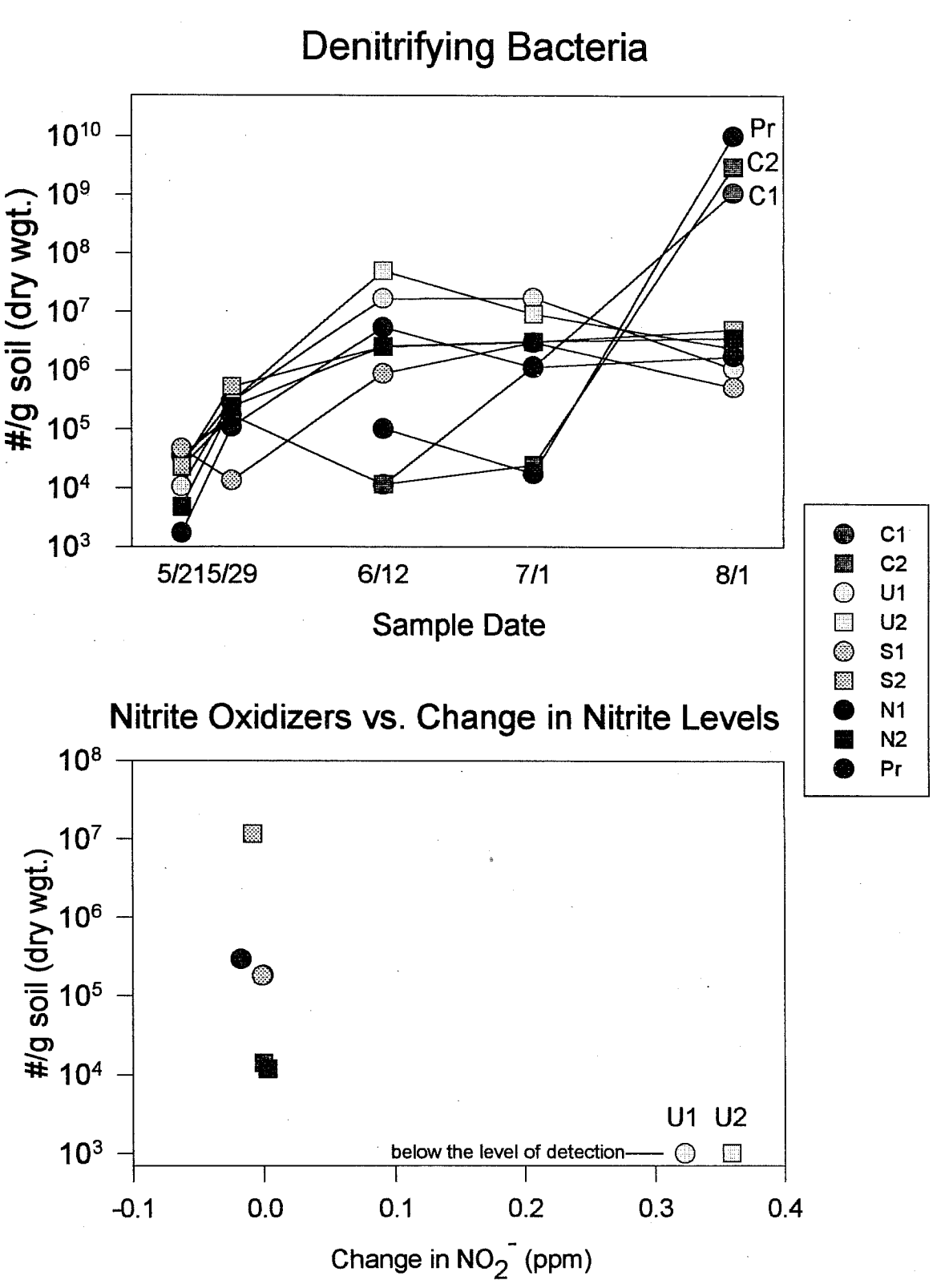


Figure 2. Nitrogen ions



X axis:change in nitrite levels from 6/12 to 7/1
Y axis: # nitrite oxidizing bacteria (MPN) on 7/1

Figure 3. Bacteria

Microbial Characterization of Soil Impacted by Gas Condensate

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ABSTRACT

Condensate liquids have contaminated soil and groundwater at two gas production sites in the Denver Basin operated by Amoco Production Co.. Extensive groundwater, soil gas and soil core data collected over past three years suggest that intrinsic bioremediation is occurring at these sites by multiple pathways including aerobic oxidation, sulfate reduction and methanogenesis. The geomicrobial evidence supporting this conclusion is presented here.

Soil cores were collected aseptically from the saturated zone in the vicinity of water table. Results of most probable number (MPN) determinations for general aerobic bacteria (GAB), sulfate reducing bacteria (SRB) and methanogens native to the soil are reported in conjunction with soil analyses for hydrocarbons and geochemical parameters such as SO_4^{2-}, NO_3^-, acetate, formate, Fe(II) and Fe(III).

INTRODUCTION

Amoco operates more than 800 natural gas wells within the Denver Basin, Colorado, which each average about 10^5 std ft^3/d (2830 std m^3/d) of gas and less than about 3 barrels/d of associated water and condensate liquids. Condensate has been found to contaminate soil and groundwater at certain sites and Amoco has sought a low-cost alternative to active remediation of these sites wherein acceptable environmental conditions would be restored. Natural or intrinsic bioremediation is one such option. This option recognizes that indigenous microorganisms in the subsurface can degrade hydrocarbons when critical environmental factors are not limiting (e.g. nutrients, temperature, moisture, pH, salinity, and electron acceptor availability). Recently, researchers have convincingly demonstrated the natural attenuation of hydrocarbon plumes in groundwater under both aerobic and anaerobic conditions (1, 2). Oxygen, nitrate, Fe(III) oxides, sulfate and carbon dioxide have all been identified as terminal electron acceptors for the biochemical oxidation of hydrocarbons (3-7).

In-depth field monitoring has been carried out since July, 1993, at two sites situated near the Platte River in agricultural areas near Ft. Lupton, Colorado. These sites (KPU-2 and BPU-2) are in close proximity to surface receptors, the aquifer material is highly permeable (gravely sands, sands, and silty sands) and the shallow water table (3-5 ft) fluctuates greatly with seasonal irrigation. Extensive groundwater, soil gas and soil core data collected over past three years and concurrent laboratory microcosm studies suggest that intrinsic bioremediation

is occurring at these sites by multiple pathways including aerobic oxidation, sulfate reduction and methanogenesis (8, 9).

In the past, attempts have been made to correlate the geochemistry with the geomicrobial parameters at hydrocarbon-contaminated sites (10, 11) and also collect data on the native microbial consortia to reflect the potential for contaminant degradation (12). We report here a microbial characterization study of the BPU-2 site. The purpose of this study was to demonstrate distinct differences in the populations of microbial consortia responsible for sulfate reduction and methanogenesis in the uncontaminated and contaminated regions at this site. The results of this study provide the geomicrobial evidence to support the hypothesis that intrinsic bioremediation of gas-condensate hydrocarbons is occurring at these sites by sulfate reducing and methanogenic pathways.

MATERIALS AND METHODS

Soil Core Sampling

Four soil cores (1 core from the uncontaminated zone upgradient and three cores within a five-spot well pattern in the plume zone) were collected at BPU-2 in the first week of November, 1995 (Figure 1). A hollow stem auger was used to drill a 10-cm diameter hole to about 15 cm above the water table. From this depth downwards, a percussion gouge with a core sampler assembly was driven down to obtain a continuous soil core. A sterilized PVC tube (6.3-cm outer diameter, 99 cm long) fitted with a core catcher at the bottom was employed to obtain soil

cores aseptically. After withdrawing the core sampler, it was cut into 15 cm long sections with a hacksaw and end-capped with sterilized PVC caps and sealed with duct tape on both the ends. These sections were immediately stored at 1 C.

Inoculum Preparation

The soil cores were transferred to an anaerobic glove box (Coy Laboratory Products Inc., Ann Arbor, MI) one at a time. From both the ends, about 2.5 cm of soil was discarded. The central portion of the remaining soil was carved out carefully (to avoid contamination from the surface of the PVC tube) and thoroughly mixed in a 250-mL beaker using a stainless steel spatula. Ten g of this soil was suspended in 90 g of pre-reduced methanogenic mineral salts solution (13) in a 100-mL serum bottle which was immediately sealed and crimped. All of the glassware, spatula and Balch stopper (Bellco Glass Inc., Vineland, NJ) were sterilized prior to use to ensure aseptic handling of the soil. This suspension was used as an inoculum of indigenous microorganisms for MPN enumerations of general aerobic bacteria (GAB), sulfate reducing bacteria (SRB) and methanogens.

Inorganic and Organic Analyses

Once the microbial inoculum was prepared, the rest of the soil was split into following subsamples for analyses of hydrocarbons and inorganic species. Forty g soil was suspended with 25 g methylene chloride to extract soil hydrocarbons which were analyzed as BTEX and total petroleum hydrocarbons (TPH) by gas chromatography. Soil acetate, formate, sulfate and nitrate were extracted by contacting 25 g soil with 300 parts per million by weight (ppmw)

aqueous potassium bromide and quantified by ion chromatography. Fifteen g soil was extracted with deaerated 1 N hydrochloric acid for Fe(II) and total Fe analyses by colorimetry. Soil moisture content was determined by drying 10 g of soil at 105 C. Extraction protocols and analytical procedures have been described elsewhere (8, 9).

Microbial Enumerations

All assays were conducted after incubation at 30 C. A three-tube most probable number (MPN) procedure was used for enumeration of GAB and SRB using a series of 10 dilutions (14). GAB were assayed using a nutrient medium containing dextrose (1 g/L) and scored for presence of turbidity in the vials after 7-10 days (15). SRB were enumerated using a RST-II medium containing 450 mg/L sulfate with lactate (2.4 g/L sodium lactate) as a carbon source (16). SRB were scored for sulfide production as observed by blackening of the medium and an iron brad after 21 days. In the case of some samples, which were extremely black indicating the presence of FeS, a sterile control series was run to ascertain that the blackening was not due to dilution of sulfide in the inoculum. Methanogens were assayed by single tube serial dilution method (8 dilutions) using a sulfate-free, mineral salts medium (13) with acetate (2 g/L sodium acetate), formate (1 g/L sodium formate) and hydrogen (H_2:CO_2 80:20%, 10 psi) as potential electron donors. An identical series with the same medium but with nitrogen (N_2:CO_2 80:20%, 10 psi) was used as a control. Methanogens were scored for methane production after 60 days of incubation by analyzing 0.2 mL of the headspace sample with a Varian 3300 gas chromatograph equipped with a

Porapak Q column and a flame ionization detector using nitrogen as the carrier gas. Acetoclastic methanogens were scored from N_2-CO_2 tubes for methane production in excess of 3.08 % (10 % excess over stoichiometric utilization of formate alone). Hydrogen/formate utilizing methanogens were similarly scored from H_2-CO_2 tubes for methane in excess of 21 % (methane concentration corresponding to stoichiometric utilization of all hydrogen in the headspace) or methane in excess of 50 % over that in N_2-CO_2 tubes.

RESULTS

Groundwater data collected over more than two years indicate that in the hydrocarbon contaminated zone, the aquifer is anaerobic, sulfate is completely depleted, Fe(II) concentrations are elevated and that the contamination is largely confined to shallow depths in the vicinity of water table (8). Soil core data in addition to confirming these findings also indicate a net reduction in the hydrocarbon content but show finite levels of sulfate in the plume zone. A soil gas survey conducted in September, 1995 indicated methane levels as high as 45 % near the water table in the plume zone (8). These observations indicate that sulfate reduction and methanogenesis play a major role in hydrocarbon attenuation. The present study lends microbiological evidence for this conclusion.

Microbial Enumerations

In Figure 2, MPNs for soil cores are plotted as a function of average core depth from the water table. The water table at the time of sampling was 112 cm

below ground level. General aerobic bacteria which provide a measure of the total heterotrophic microbial population showed moderate differences between soil from control and plume as seen in Figure 2 (a). Also, the GAB levels showed no correlation with depth or with the axial distance of the soil core from the source.

In contrast, SRB and methanogenic consortia showed significant enrichments in the soil samples from the plume zone in comparison to control. SRB in plume samples exhibited one to two orders of magnitude enrichment over control samples (Figure 2(b)). SRB counts did not show any specific trend with depth nor with the axial location in plume.

In the case of both acetoclastic and H_2/formate utilizing methanogens, no methane was detected (detection limit 0.02 %) in the control samples, suggesting total absence of any methanogenic consortia in the control zone. In contrast, the plume samples showed counts as high as 10^4 to 10^9 / gm dry soil for both classes of consortia (Figures 2(c) and 2(d)). In fact, in some samples the dilution extinction was missed and the actual counts may have been higher than 10^9 /gm dry soil.

Hydrocarbons in soil

Figure 3 shows the hydrocarbon data as a function of depth from water table. Neither BTEX nor any TPH were detected in the soil cores obtained from control area. In comparison, as much as 150-300 mg/kg BTEX and 1500-3600 mg/kg TPH were observed in the soil cores from the contaminated area. Most of the contamination was confined to the zone of about 15-25 in (38-63.5 cm) below

the water table. This is in excellent agreement with the earlier observations (8). The maximum BTEX concentration decreased with an increase in the distance from source. In general, a similar trend was also seen with TPH data with the exception of BP2.

Geochemical parameters

Figure 4 shows the various geochemical parameters obtained by aqueous extraction of soil cores. Concentrations of all the analytes in the extract were corrected by considering bromide as a conservative internal standard. Ratio of bromide concentration in the extract to that in the original aqueous bromide was used as a measure of extraction efficiency. Overall extraction efficiency of 94-100 % was observed. Nitrate and acetate were below detection limit in all the samples (1 mg/L and 0.5 mg/L, respectively).

As illustrated in Figure 4(a), ratios of Fe(II) to Fe(III) for plume soil core samples (0.5 to 6) were one to two orders of magnitude higher in contrast to control soil core samples (0.01 to 0.02). This is a clear indication of Fe(III) reduction in the presence of hydrocarbons. Fe(III) reduction may be biotic (Fe(III) as an electron acceptor) or abiotic with Fe(III) being reduced by biogenic hydrogen sulfide to Fe(II) (6).

Sulfate, which is an important electron acceptor at this site exhibited an interesting pattern (Figure 4(b)). Sulfate concentrations obtained from control soil core samples (about 20 mg/kg) were lower than in the plume soil core samples (average of 60 mg/kg), but none of the samples were completely depleted of sulfate. In contrast, groundwater samples previously collected from 1-in shallow

wells, were completely depleted of sulfate in the plume but contained about 230 mg/L sulfate in the control (8).

Formate concentrations did not show any specific trend with respect to depth or presence of contamination (Figure 4(c)). Soil extract pH for plume soil samples was lower (6.8 to 7.8) compared to control soil samples (8 to 8.3), due presumably to the presence of carboxylic acids which are important intermediates of hydrocarbon biodegradation.

CONCLUSIONS

Results of microbial enumerations and geochemical parameters clearly indicate that SRB and methanogenic consortia were considerably enriched in the presence of hydrocarbon in soil. This is strong microbiological evidence consistent with the earlier conclusion that sulfate reduction and methanogenesis are important mechanisms for hydrocarbon biodegradation at this site. The extent of enrichment for methanogenic consortia was considerably more than SRB. Some of the possible explanations for these differences include different soil phase - liquid media partition coefficient for methanogens and SRB, different viability in respective MPN growth media, sulfate depletion and sulfide accumulation causing inhibition to native SRB population, etc. These soil samples are presently being analyzed for acid volatile sulfide to ascertain if sulfide inhibition of SRB is likely.

ACKNOWLEDGMENT

We gratefully acknowledge Dr. Michael McInerney at the University of Oklahoma for his helpful suggestions and access to laboratory for methane analysis during the course of this work.

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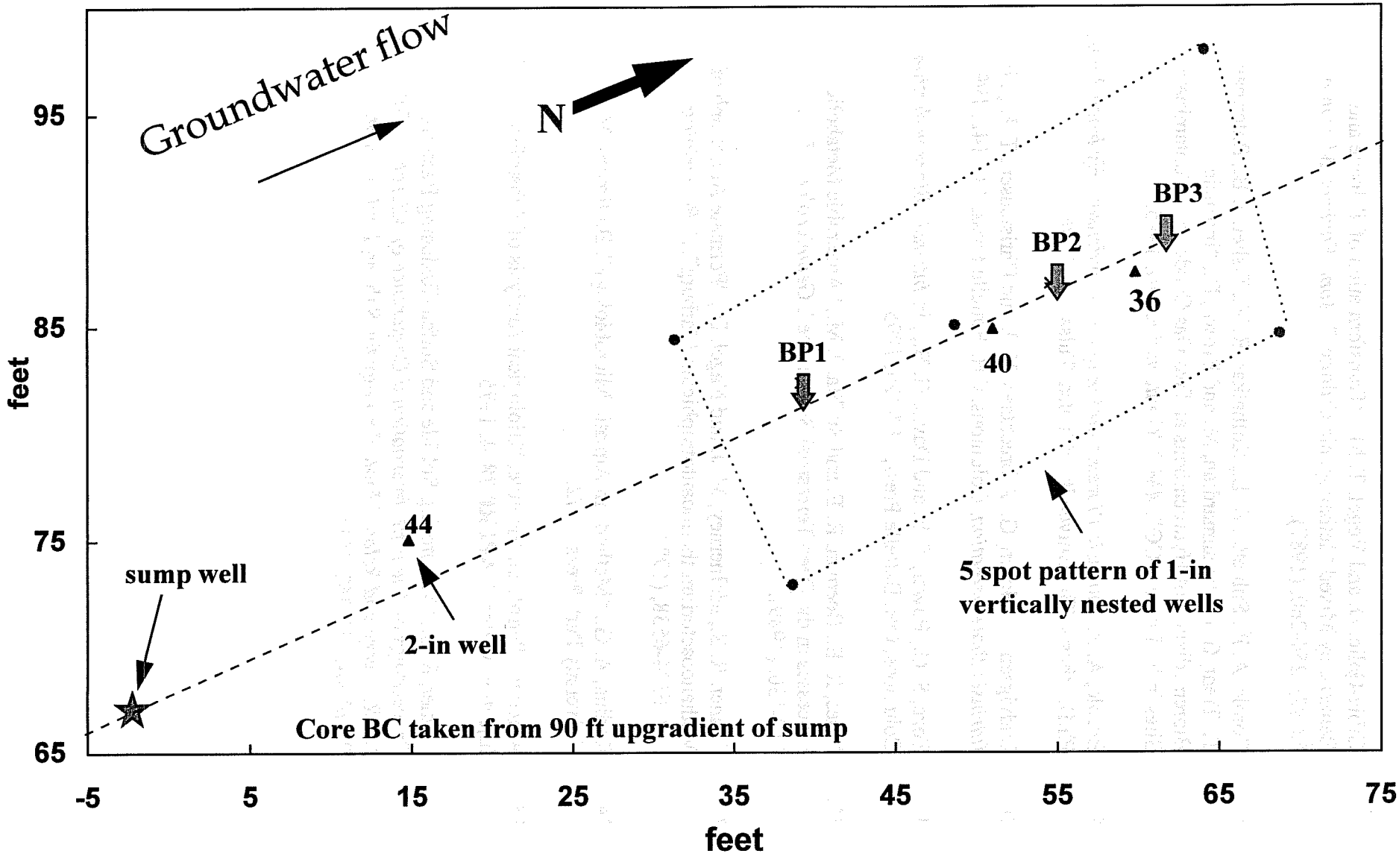

Figure 1. Soil core locations at BPU-2 site

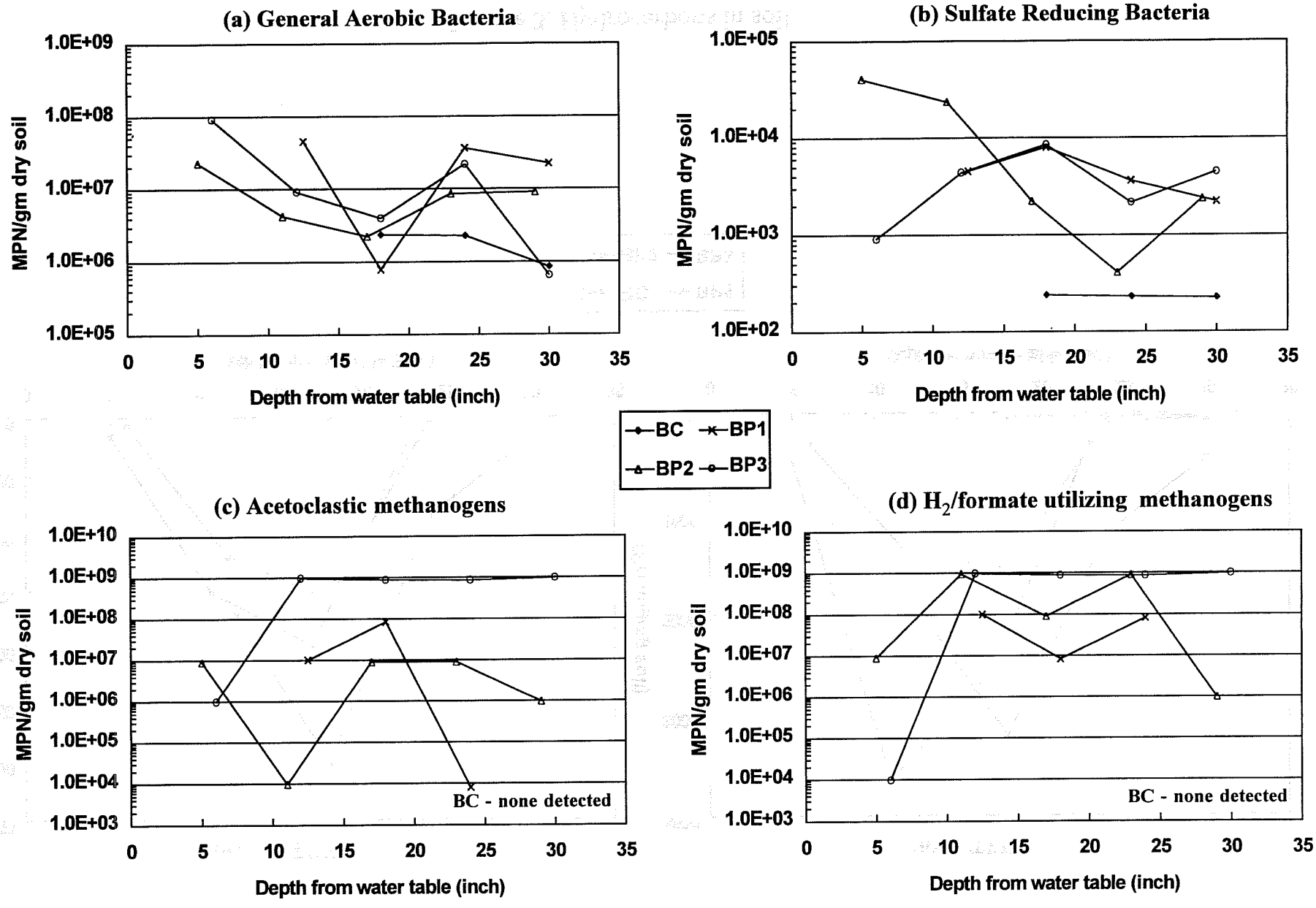

Figure 2. Geomicrobial parameters

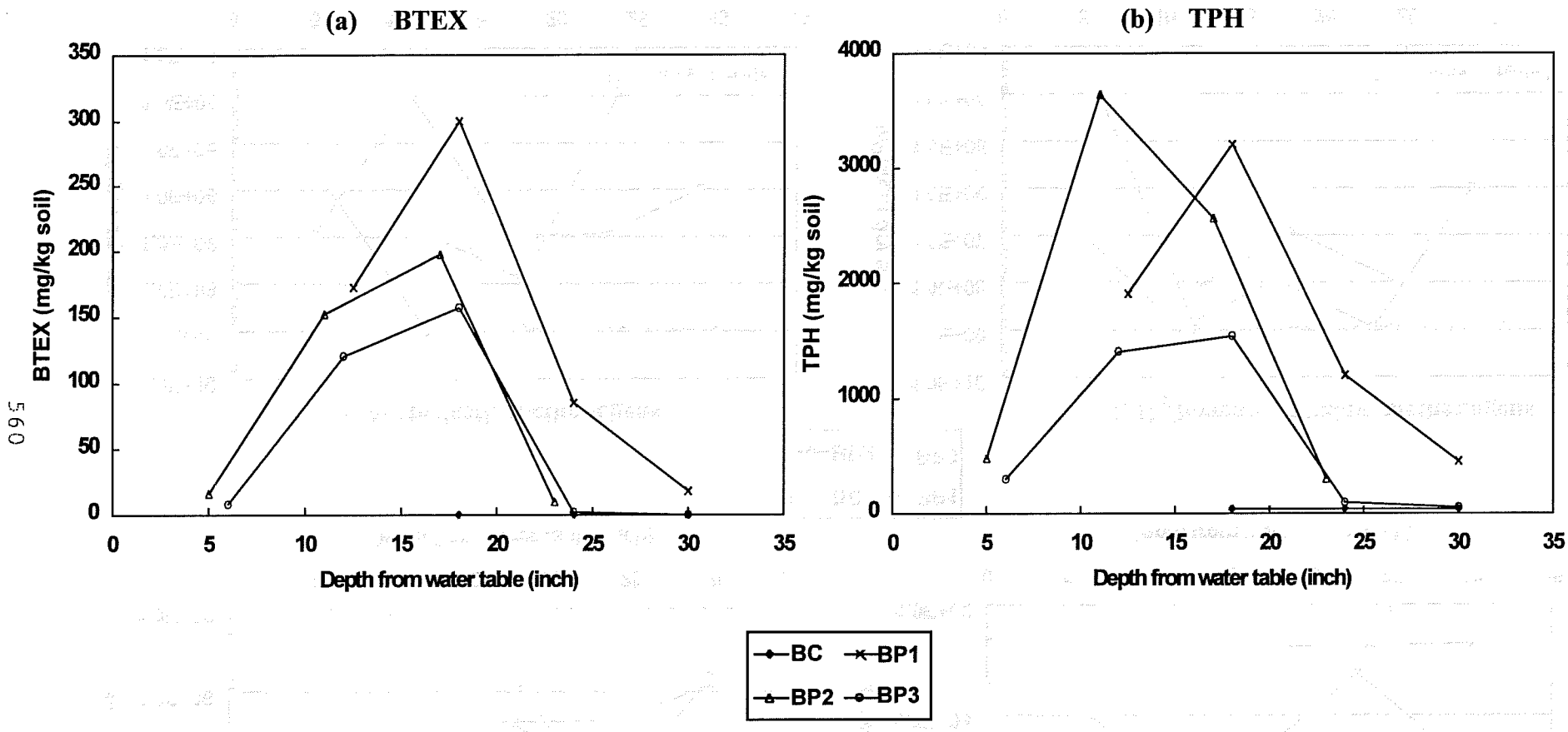

Figure 3. Hydrocarbons in soil

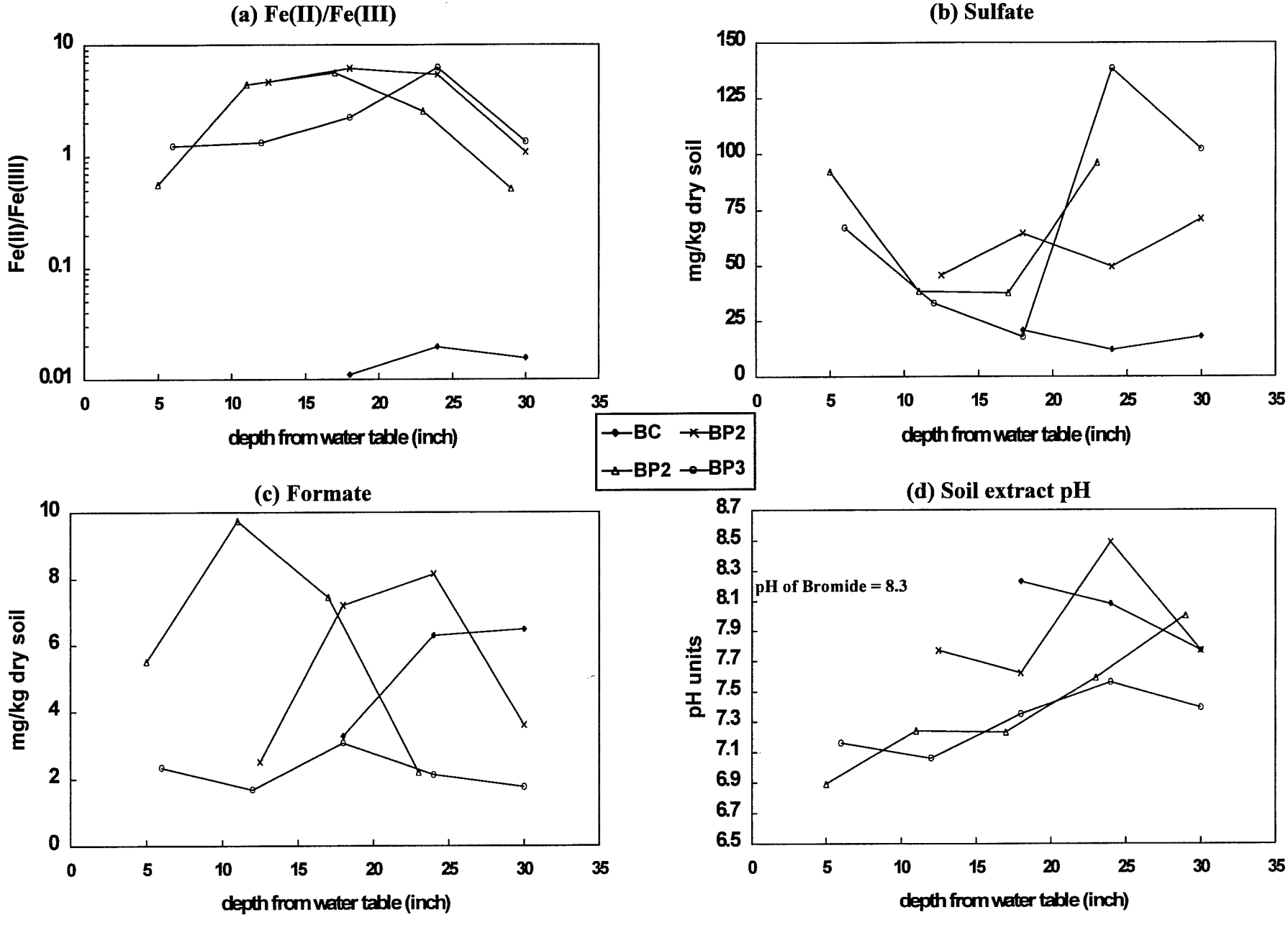

Figure 4. Geochemical parameters

Understanding the Mechanisms of Natural Attenuation of Gas Condensate Hydrocarbons : Results of Over Two Years of Field Observations

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ABSTRACT

Condensate liquids have been found to contaminate soil and groundwater at two gas production sites in the Denver Basin operated by Amoco Production Co. These sites have been closely monitored since July, 1993 to determine whether intrinsic aerobic or anaerobic bioremediation of hydrocarbons occurs at a sufficient rate and to an adequate endpoint to support a no intervention decision. Groundwater monitoring, soil gas analysis and analysis of soil cores suggest that bioremediation is occurring at these sites by multiple pathways including aerobic oxidation, sulfate reduction and methanogenesis. Results of over two years of monitoring of groundwater and soil chemistry at these sites are presented to support this conclusion.

INTRODUCTION

Condensate liquids have been found to contaminate soil and groundwater at certain natural gas production sites operated by Amoco in the Denver Basin, Colorado. Natural or intrinsic bioremediation is a low-cost approach undertaken by Amoco to address this problem. This option recognizes that indigenous subsurface microorganisms can degrade hydrocarbons under optimal conditions of nutrients, temperature, moisture, pH, salinity, and electron acceptor availability. Recently, researchers have convincingly demonstrated the natural attenuation of hydrocarbon plumes in groundwater under both aerobic and anaerobic conditions (*1, 2*). Oxygen, nitrate, Fe(III) oxides, sulfate and carbon dioxide have all been identified as terminal electron acceptors for the biochemical oxidation of hydrocarbons (*3-7*).

Amoco has initiated a study to determine whether intrinsic aerobic or anaerobic bioremediation of hydrocarbons occurs at these Denver Basin sites at a sufficient rate and to an adequate endpoint to support an intrinsic remediation option. Tasks specific to this objective are : (1) long-term groundwater and soil monitoring (initiated July, 1993) to document field hydrocarbon losses and bioactivity over time (quarterly sampling events for 5 to 6 years for groundwater; annual sampling events for soils); (2) laboratory verification of hydrocarbon degradation by field microorganisms and identification of primary biodegradation mechanisms (September, 1993 to December, 1995); and (3) microbiological characterization of the sites to understand the spatial utilization of electron acceptors in and around the hydrocarbon plume (initiated November, 1995).

Here we report the results of over two years of groundwater and soil monitoring (July, 1993 to November, 1995) at one of these sites (KPU-2). The implications of these data to natural attenuation of hydrocarbons are discussed.

SITE CHARACTERIZATION AND MONITORING

In-depth field monitoring has been carried out since July, 1993, at two sites situated near the Platte River in agricultural areas near Ft. Lupton, Colorado. These sites (KPU-2 and BPU-2) are in close proximity to surface receptors, the aquifer material is highly permeable (gravely sands, sands, and silty sands) and the water table fluctuates greatly with seasonal irrigation. Extensive groundwater, soil gas and soil core data collected over the past two years and concurrent laboratory microcosm studies suggest that intrinsic bioremediation is occurring at these sites by multiple pathways including aerobic oxidation, sulfate reduction and methanogenesis (8, 9).

Groundwater Monitoring

Based on an initial soil gas survey (10), permanent groundwater monitoring wells were installed to determine the extent of hydrocarbon loss and the degree of bioactivity over time. Figure 1 shows the locations of 1-in (2.54-cm) O.D. vertically nested monitoring wells that were installed in five-spot patterns within both the plume and control areas of the KPU-2 site. This monitoring arrangement was adopted to define areal and vertical variations of hydrocarbon and electron acceptor concentrations in groundwater. Additional 2-in (5.1-cm) O.D. monitoring wells were placed along the

longitudinal axis of predominant groundwater flow to monitor plume migration and electron acceptor transport.

To adequately address hydraulic modeling requirements and thereby ultimately assess the role of abiotic mechanisms (e.g., dispersion, advection) in hydrocarbon loss, both the downgradient contaminated area and the upgradient uncontaminated area were contained within a larger hydraulic five-spot monitoring pattern. In addition to these pressure monitoring wells, the axial 2-in (5.1-cm) wells were also used to measure water level during groundwater sampling. More details about the well installation are described earlier (9,10).

Soil Core Sampling

Soil cores were obtained from each site in November, 1993 to document the initial soil hydrocarbon and electron acceptor distributions. Four cores were taken from within each control and plume area. Coring locations were situated approximately halfway between the center and corner well clusters in each pattern quadrant. Continuous cores were obtained with a 2-in (5.1 cm) split-spoon sampler from the surface to a total depth of 15 ft (4.6 m). Core samples were composited at 1.5 ft (45.7 cm) intervals and stored in a reduced oxygen environment at 4 C until requisite analyses could be performed. A second set of cores was collected in November, 1994 to document changes in the hydrocarbon concentrations. These cores were taken within 1 m of the 1993 coring locations. To minimize disturbance, the cores taken in November, 1994 were obtained by vibracoring. In the vibracoring operation, continuous cores were obtained in a 3-in (7.6-cm) acrylic sleeve from surface to a total planned depth of 10 ft (3.0 m). The coring done in November, 1995 was again done with a split spoon sampler to a total depth of 15 ft

(4.5 m). Material from these cores was composited and analyzed in the same manner each year.

Analytical

Individual groundwater samples were collected and analyzed for inorganic constituents such as nitrate, sulfate, total alkalinity (as mg/L $CaCO_3$), Fe(II) as well as BTEX and TPH (10).

Soil solids were analyzed for moisture content, acid extractable Fe(II) and Fe(III), porosity, bulk density and saturated paste pH, nitrate, sulfate as well as BTEX and TPH. Details of the preparation of saturated soil paste and the individual analyses are as described earlier (10, 11).

RESULTS

Groundwater

Based on the baseline groundwater data collected in the first week of November, 1993, it was inferred that the contamination was largely confined to shallow depths and that sulfate reduction was an important mechanism in hydrocarbon attenuation at this site (10, 11). The importance of sulfate as an electron acceptor was also suggested by microcosm studies undertaken in the laboratory (8, 12). Additional sampling since that time continues to support sulfate reduction as an important pathway for the attenuation of hydrocarbons at the site.

Initial groundwater data indicated that BTEX and TPH were confined primarily to the shallow well depth (3.5 to 5 ft below grade) (9). At this depth, various electron

acceptors including sulfate, nitrate and dissolved oxygen (DO) exhibited diminished concentrations in the plume versus the control zone. Similarly, concentrations of Fe(II), a product of Fe(III) reduction, and total alkalinity (mainly bicarbonate) were higher. Water samples collected from intermediate depth wells in the plume area showed similar but less pronounced trends in hydrocarbon and electron acceptor concentrations. Deep well data indicated non-detectable levels of hydrocarbons in both plume and control. Since most of the activity is occurring at shallow depths, further discussion will be restricted to only the shallow-screened wells.

BTEX data are plotted in Figure 2 for shallow-screened, 1-in (2.54-cm) wells using complete data collected from November, 1993 through November, 1995. BTEX was completely absent from wells upgradient of sump (i.e. control zone), whereas, considerable concentrations of BTEX (20 to 40 mg/L) were detected in the downgradient wells (i.e. plume zone). Extremely high BTEX concentrations seen in wells 14 and 17 in February, 1994 were due to sample collected from a vapor point since the water table was below the screen. These were point samples as opposed to volume averaged samples over the 18-in (45.7-cm) screened interval for the other samples. Lower values of BTEX were observed in the sump compared to plume indicating that this region did not have any further source of contamination such as a NAPL (Non Aqueous Phase Liquid).

A similar plot for sulfate concentrations (Figure 3) indicates considerably diminished sulfate in the plume zone associated with the presence of hydrocarbons, whereas wells in the control zone had sulfate on the order of 230 mg/L. In addition, all the groundwater samples from the wells in plume zone had a strong hydrogen sulfide smell indicating active sulfate reduction.

Similarly, increased Fe(II) and total alkalinity as well as reduced DO were observed in the plume zone compared to in the control zone (data not shown). Increased levels of Fe(II) in the plume (4 to 6 mg/L compared to near zero concentrations in control) indicate Fe(III) reduction occurring in this zone, although the utilization of Fe(III) as electron acceptor cannot be quantified because of its low solubility. Fe(III) reduction may be biotic or abiotic. Hydrogen sulfide produced by biological sulfate reduction can reduce Fe(III) to Fe(II) and precipitate it as iron sulfide (*6*).

Dissolved oxygen in the plume ranged from 0.25 to 1.4 mg/L in the absence of sulfate. Bicarbonate, the major component of total alkalinity, is a product of biodegradation of hydrocarbons. Considerably higher values of alkalinity in the plume (average 600 mg/L $CaCO_3$ compared to 300 mg/L in control) strongly suggest that biodegradation of hydrocarbons is occurring in the plume.

As seen in Figure 2, no clear decrease in BTEX concentrations in groundwater has been observed to date (November, 1995) due presumably to replenishment of dissolved hydrocarbons from a sink of sorbed hydrocarbons and water table fluctuations. Individual water level measurements from the 2-in (5.1-cm) axial wells showed water table fluctuations of 2.5 to 3 ft (0.76 to 0.91 m) with the water table being higher during summer (June to September) and lower during winter (November to March) (data not shown). Based on the water level data obtained from these wells, it was evident that the local gradient exhibited fourfold seasonal variations. Higher gradient was seen during summer and lower gradient during winter. This has important bearing on relative magnitudes of hydrocarbon mobility and attenuation rate. During winter, when biological activity would be slower, mobility of dissolved hydrocarbons would be higher

due to higher groundwater velocity, causing the dissolved plume to migrate at a higher rate. The reverse phenomena would take place during summer resulting into increased attenuation in summer.

Finally, axial monitoring well data indicated that highly soluble BTEX components had migrated a distance of only 165 ft (50.3 m) from the source over an estimated 20-year time period and sulfate and Fe(II) concentrations were at background levels at this distance (data not shown).

In summary, the following observations are made on the basis of groundwater data acquired to date. The aerobic biodegradation potential of hydrocarbon appears limited due to uniformly low DO concentrations (1.4 mg/L or less) throughout the investigated area; however, the role of oxygen at the edge of the plume is potentially important. Nitrate is present due to agricultural applications of fertilizer but, because of its low concentration, has limited potential for hydrocarbon degradation (11). In contrast, the utilization of sulfate appears significant. Background concentrations are on the order of 230 mg/L, whereas sulfate is practically absent in the shallow area containing hydrocarbons. Given the large initial concentrations of sulfate and its favorable stoichiometric utilization for hydrocarbon degradation, it appears that sulfate reduction is a major means of hydrocarbon remediation at these sites. Moreover, concentrations of sulfate observed in June, 1995 sampling show that a substantial amount of sulfate was transported by infiltration of rainwater and that the rate of sulfate consumption in the hydrocarbon contaminated groundwater exceeded the rate of supply by infiltration. This sampling was conducted immediately after a period of persistent heavy rainfall. In the control area at KPU-2, background sulfate levels in the shallow wells had nearly doubled

(average of 5 wells = 418 mg/L sulfate), whereas sulfate concentrations for intermediate and deep wells were comparable to those observed previously. In contrast, sulfate concentrations in shallow wells from plume area showed an absence of sulfate.

Soil Cores

Soil core analyses for total iron, Fe(II), BTEX, and TPH were performed on composited samples from each 1.5 ft (45.7 cm) interval. Within the plume area (Figure 4), BTEX was consistently present in soil cores, but confined to an approximate 3 ft (0.91 m) interval at the water table / air interface, in contrast to non-detect levels observed in all control area soil cores. Soil BTEX concentrations have considerably reduced over the past two years. Since BTEX concentrations observed in groundwater monitoring wells have remained essentially unchanged, this is interpreted to indicate that the total hydrocarbon inventory at this site is being decidedly reduced by natural attenuation. Soil TPH also was confined near the water table but did not exhibit attenuation similar to BTEX (data not shown). As discussed earlier, BTEX concentrations in the groundwater did not show a temporal trend, due to the presence of a residual hydrocarbon phase (Figure 2). Also, no specific movement of the dissolved hydrocarbon plume was indicated by the groundwater data from 2-in (5.1-cm) wells. Once the BTEX inventory diminishes, groundwater BTEX concentrations may start decreasing and the plume also may start shrinking.

Soil sulfate concentrations and Fe(II)/Fe(III) ratios obtained by saturated paste extract method (11) showed distinct differences between plume and control zone samples (data not shown). Sulfate concentrations were lower in the plume region (4 to 100 mg/kg compared to 100 mg/kg and above for control). Although, sulfate was absent in many of

the 1-in (2.54-cm) shallow-screened wells in the plume, soil still contained sulfate in mineral form. Dissolution of sulfate minerals might have controlled the supply of sulfate to the groundwater. No specific change was observed in sulfate concentrations in the soil cores from November, 1993 to November, 1994 (data not shown).

When hydrocarbons were present, Fe(II)/Fe(III) ratios in soils were higher. This is an indication of Fe(III) reduction in the presence of hydrocarbons as a result of anaerobic biodegradation and further supports the hypothesis that intrinsic bioremediation of hydrocarbons is occurring at these sites by multiple pathways.

Finally, visual inspection of soil cores showed a significant accumulation of a black precipitate (acid volatile sulfide) associated solely with the presence of hydrocarbons. The accumulation of iron sulfide (FeS) in the presence of hydrocarbons is consistent with the anaerobic biodegradation of hydrocarbons by sulfate reduction (*6*).

CONCLUSIONS

At the sites investigated, intrinsic aerobic and anaerobic bioremediation play a strong role in attenuating hydrocarbons. Even though the sites are old (> 20 years), hydrocarbons are laterally and vertically confined to a small portion of the total aquifer. Further, there is strong geochemical evidence of both aerobic and anaerobic bioactivity. Oxygen is much depleted and carbon dioxide is much elevated in the soil gas immediately overlying the groundwater associated with the hydrocarbon plume. Groundwater that is immediately associated with the hydrocarbon plume shows depleted

levels of both nitrate and sulfate compared to groundwater from the upgradient uncontaminated zone.

Soils associated with hydrocarbons show abundant iron sulfide production. Although sulfate is depleted in groundwater associated with hydrocarbons, sulfate remains available as an electron acceptor by means of diffusion from the surrounding aquifer, by dissolution of sulfate from the solid phase, and by importation of sulfate by infiltration of rainwater. Potentially, sulfate reduction could be accelerated in the hydrocarbon impacted areas through the addition of sulfate.

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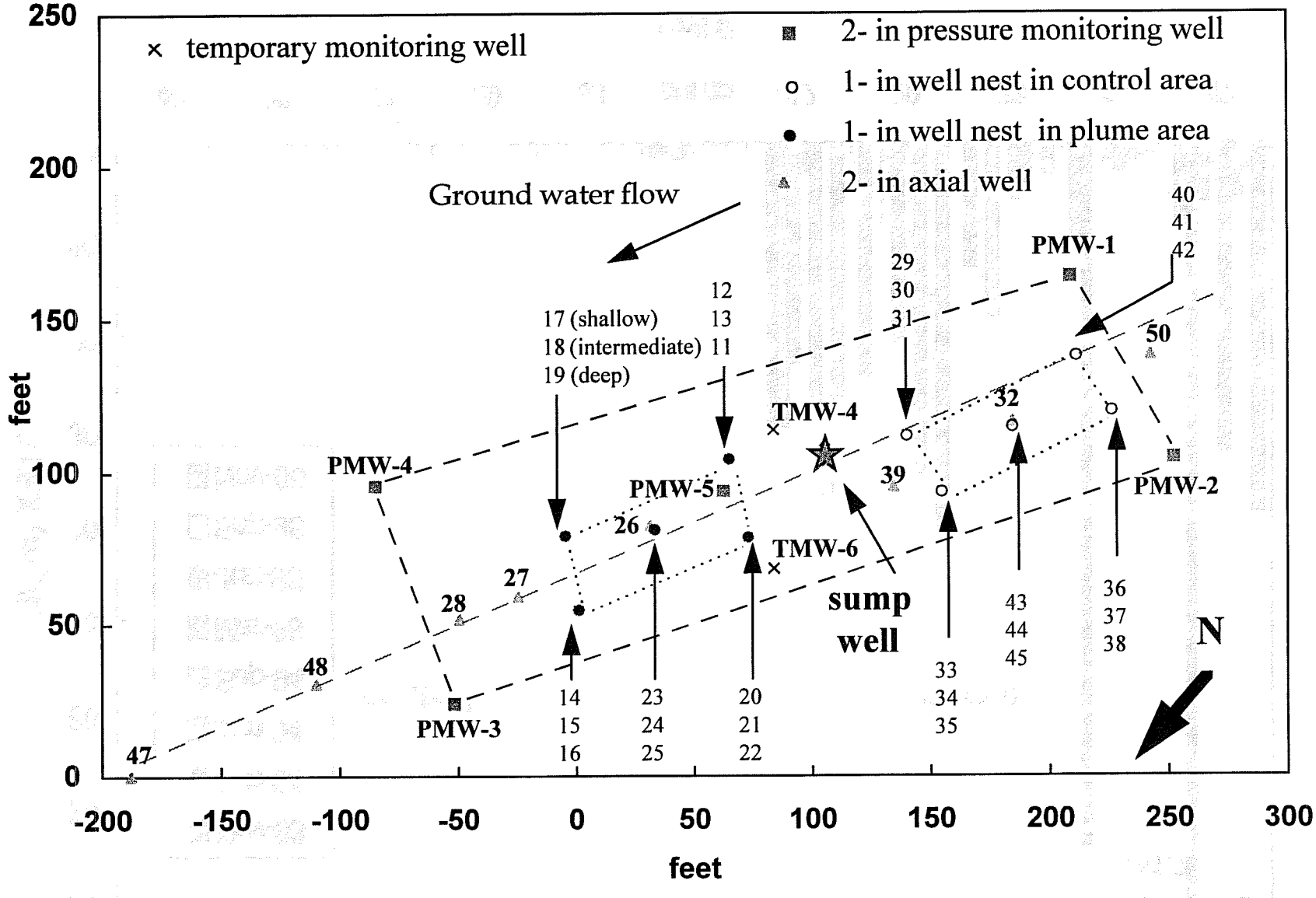

Figure 1. Site map of KPU-2

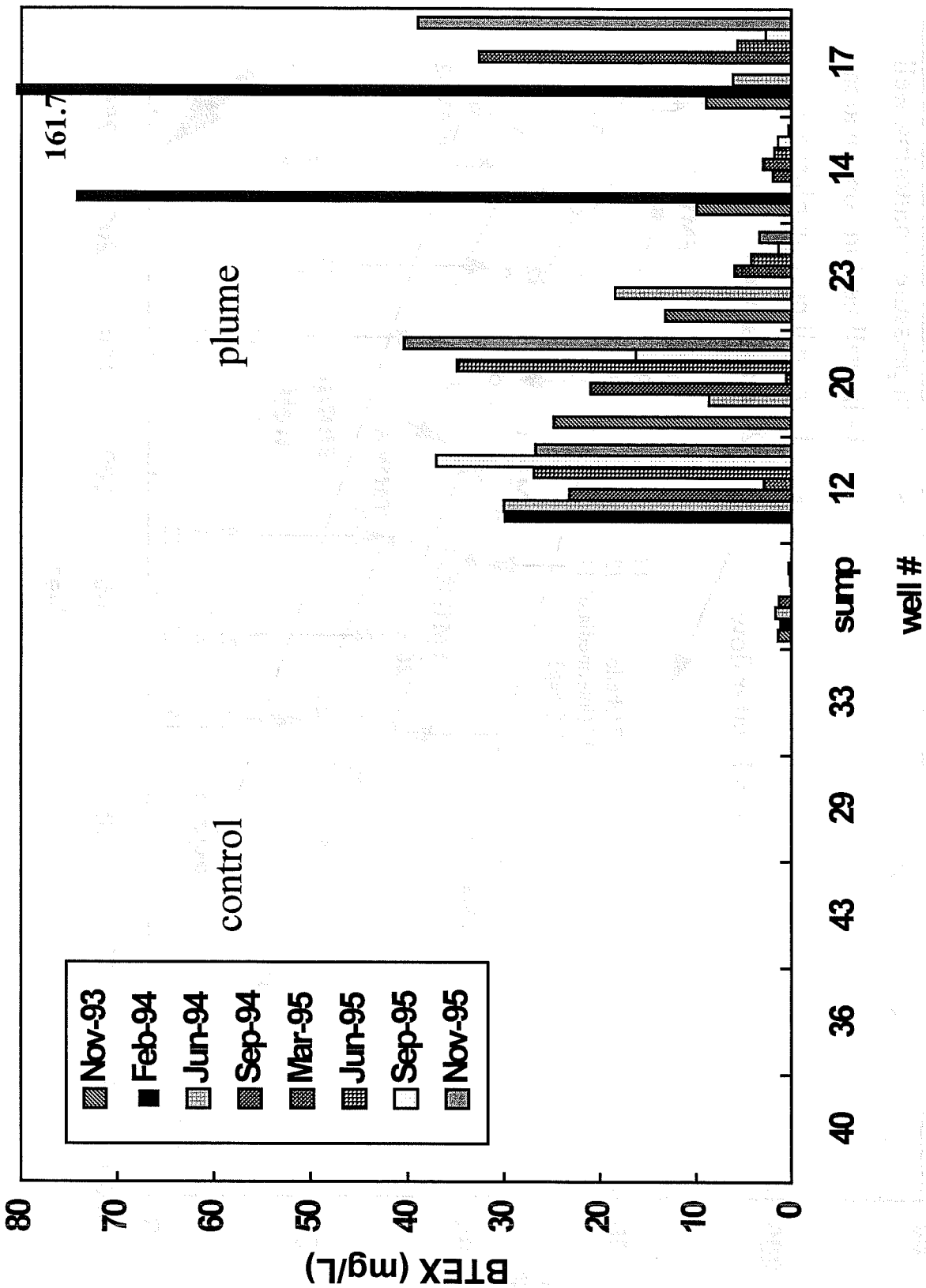

Figure 2. BTEX in 1-in shallow wells

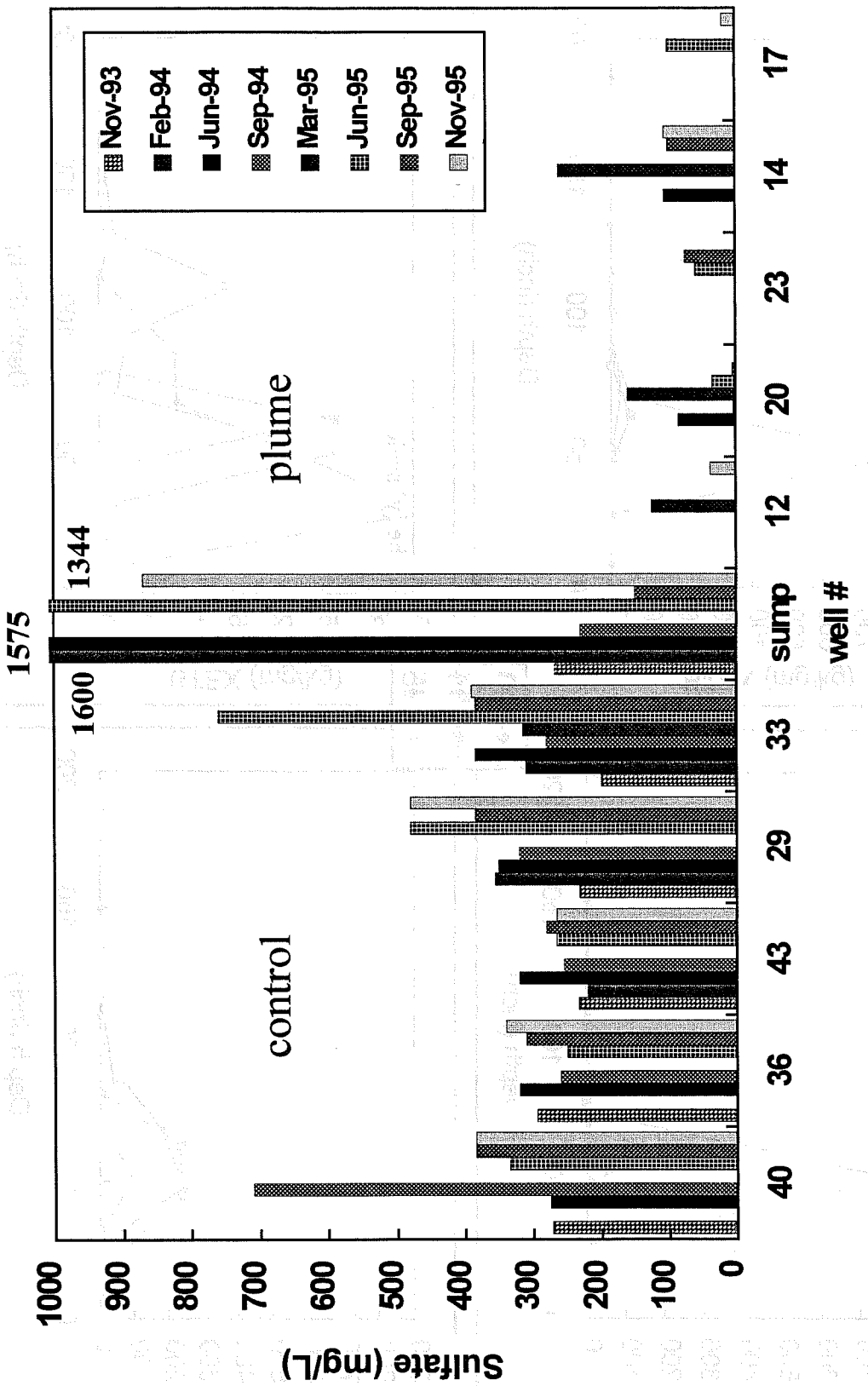

Figure 3. Sulfate in 1-in shallow wells

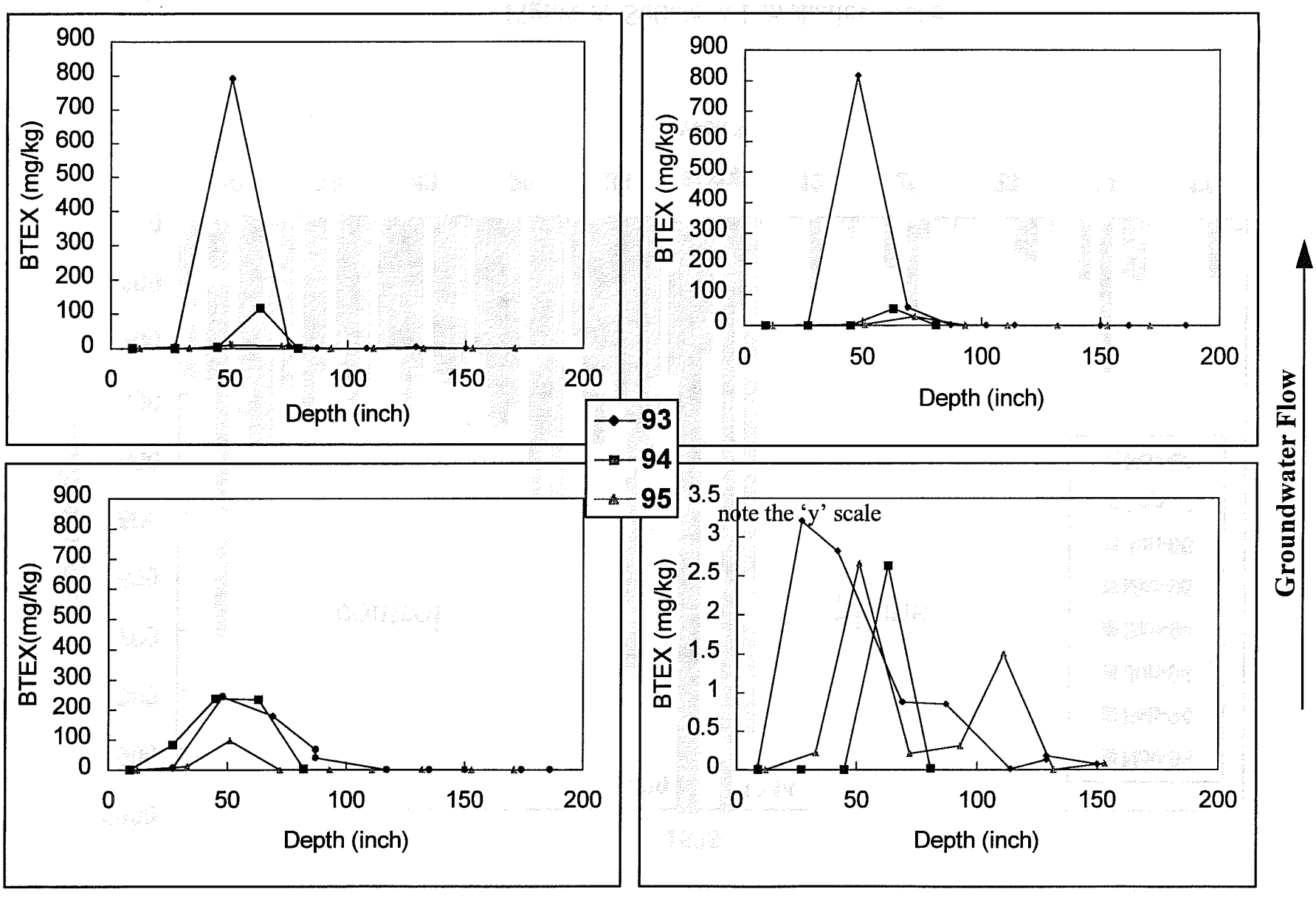

Figure 4. Soil core BTEX in plume region

The Long Term Effects of Crude Oil Contamination and Bioremediation, a Study of Soil Toxicity, Plant Diversity, and Nematode Communities

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In 1992, a field experiment was performed to determine the ability of the Microtox^{R} Toxicity Bioassay to monitor the progress of petroleum bioremediation. The outdoor lysimeters are located at the Amoco Production Research Environmental Test Facility in NE Oklahoma and were constructed identically, each being an independent, fully lined concrete bunker (9 x 9 x 3 feet deep) possessing a water drainage pipe. All three were filled with uncontaminated soil from a single location and received the following treatments: the C or Control plot was untreated, the O or Oil plot was sprayed with crude oil, and the OF or Oil and Fertilized plot was also sprayed with crude oil and then mechanically tilled and watered for 190 days. At the conclusion of the analysis, the site was abandoned. In 1995, the site was resampled; this report is a portion of the large, multi-part resampling.

A plant dry-biomass and species diversity study reveals the effects of the residual toxic contamination in the O plot and the lack of contamination in either the C or OF plots. These findings are supported by a series of Microtox^{R} analyses performed on soil taken at the time of the plant and nematode studies. The nematode analysis included the identification of the organisms, and a low diversity index within the O plot is again attributed to continued contamination and is similar to the contamination response of the plants in this plot. In addition, the placement of fertilizer to the OF plot shows an impact on the maturity index of the nematodes. Thus, these three portions of the larger study reflect the residual effects of not only petroleum contamination but also the remediation of this contamination.

INTRODUCTION

In the last two decades, an extensive amount of work has been performed in many areas of science in an attempt to design systems which will safely remove harmful pollutants from soil and water. Along with this work came a variety of techniques developed to monitor the progress of the implemented bioremediation procedures. Such tests included various lab or field parameters to determine the success or failure of a bioremediation project (1,2,3). These tests have traditionally concentrated their efforts on the quantitative measure of contaminant removal as well as the ability of certain inoculated indicator organisms to survive and thrive in the once contaminated site (4). Questions can be raised, however, as to the ability of these tests to provide a true picture of the effects of a bioremediation procedure.

Perhaps the most basic method to observe effects of site manipulation is to return to the site and measure various intrinsic parameters which will be then used to make conclusions. In this study, nematode community structure, soil toxicity measurements, and indigenous plant biomass and species diversity analyses were used to observe some of the residual effects of a controlled crude oil soil contamination and remediation.

SITE HISTORY

The research site for this experiment is part of the Amoco Production Company Environmental Research Facility in Rogers County, Oklahoma. Initially established in 1992 to test the ability of the Microtox^{R} bioassay to monitor the progress of a managed petroleum bioremediation project, the site consists of three identical reinforced concrete lysimeters measuring 9.1 feet x 9.1 feet x 3 feet deep (inside dimensions) placed into the Eastern side of a small hill (5) . Each lysimeter is fully lined and contains a drainage pipe leading into an impoundment (Fig. 1).

In 1992, each of the three lysimeters was filled with 9.2 cubic yards of uncontaminated soil of the Okay Series type collected in East Tulsa County, Oklahoma (5,6). The first lysimeter (which will be referred to as the Control or "C" plot) was left as is. The second (the Oil or "O" plot) and the third (Oil and Fertilizer or "OF" plot) lysimeters were contaminated with 21 gallons (79,499 cm^3) each of Michigan Silurian Reef crude oil which was sprayed onto the plots and then tilled to a depth of one foot (5). The OF Plot then received an additional treatment of fertilizer with a NPK ratio of 4:1:1, and weekly watering and tilling treatments (5). All three plots were covered with a waterproof tarpaulin for the 190 day duration of the study. However, the OF plot did have the tarp removed once a week

for tilling and then replaced. After the conclusion of the experiment, the lysimeters were uncovered and abandoned.

MATERIALS AND METHODS

SOIL SAMPLING

For each of the three lysimeters, five three-foot soil cores were randomly taken for sampling. The coring device consisted of sterilized aluminum pipe, 0.1 inches thick with an inner diameter of 1.2 inches. Immediately after the removal of each core from the ground, the pipe was sealed with a sterile, tightly fitting, aluminum cap and returned to the lab where each of the 15 cores was sterily divided into three sections: Level 1= surface to 3" deep, Level 2 = 3" to 12" deep, and Level 3 = 12" to the bottom of the core.

On the same day as the sampling, the soil from each level of each of the five cores for each lysimeter was sterily composited in such a way as to result in a total of nine samples representing each of the three levels of each of the three plots. It is from these nine samples that portions were removed for nematode community, soil chemical, and Microtox^{R} analyses.

SOIL CHEMICAL AND PLANT ANALYSIS

Soil from each of the nine samples was sent to Soil Analytical Services in College Station, Texas for analysis (Table 1). Only the TPH (IR and GC), NO_3, and NH_4 values are reported here.

Within one week of the soil core samples being taken, plants representative of each type found growing on the lysimeters were removed with their roots and returned to the lab where they were dried and pressed in preparation to being identified (Table 2) (7,8). Each plot was then denuded of all plant roots and shoots. These were returned to the lab and spread on drying tables after being cleaned of dirt and debris, keeping the plants from each plot separate from those of the other two. They dried for a period of three weeks at room temperature, having air circulating above, below, and through the matter. The dried plants were then bagged according to which of the three plots they originated from and weighed, including the weight of the dried plants being pressed for identification (7).

EVALUATION OF SOIL TOXICITY

The Microtox^{R} bioassay was chosen to evaluate the toxicity of the soil samples (Table 1). Microtox^{R} utilizes the bioluminescent property of the bacterium *Vibrio fischeri* to monitor the degree of toxicity via changes in light output which are in direct relation to the respiration activity of the cells (9,10). As the toxicity of the sample increases, lower concentrations are needed to decrease the respiration rate (and hence the amount of light given off) of the bacteria.

The typical parameter that a user of the Microtox^{R} system looks for and reports is called the Effective Concentration of 50%, or simply, EC50. This value is the extrapolated sample concentration where the amount of light produced by the bacteria in the absence of sample is decreased by 50% (10). In some cases such as either extremely low or high toxicity, the Basic Test, which is the initial assessment and analyses up to 45% of sample concentration, may not be testing the sample in the range of concentrations which are necessary for EC50 extrapolations. An additional test performed for this study was the 100% Test which allows for target light output decreases to be calculated for very non-toxic sample because the highest sample concentration tested is 90%.

Samples used for both the Basic and 100% Tests were taken from the nine composite samples used for all other tests. The soil was placed into small plastic jars with plastic screw lids and stored at 4 degrees Celsius until use. To make a liquid extraction for testing, 1.4 grams of soil were taken from the center of the jar and added to 14 ml of Microtox^{R} Solid Phase Diluent in a 15 ml centrifuge tube (11). The tubes were then sealed with Parafilm^{R} and placed on a rotator for 24 (+/- 2) hours. The mixture was then spun for 20 minutes at 9,000 rpm in a microcentrifuge and the supernatant drawn off. The supernatant was then tested to ensure that it was between a pH of 6.0 and 8.0 and if not, was adjusted to be so (9). Ten ml of extraction was pipetted into a clean, new 10ml borasilicate glass vial and sealed with a Teflon^{R}-lined screw-top lid which was also Parafilmed^{R}. These extractions were stored at 4 degrees C until use (always within 24 hours of preparation). For each of the nine samples, the Microtox^{R} Basic Test Protocol was followed exactly, and when the results of the Basic Test were extrapolated for each sample, a 100% Test was performed on those samples which had not shown an EC50 value below 45% of sample concentration. The protocols for the Microtox^{R} 100% Test were followed exactly.

In accordance with Microtox^{R} guidelines, a phenol standard was prepared and used at the beginning of each testing session to ensure the quality of the equipment and testing procedure (12).

NEMATODE ANALYSIS

Soil samples were placed on ice and shipped to Dr. Tim Todd at Kansas State University . These small roundworms are important in soil nutrient cycling and can be predators of soil bacteria and fungi. Identification of genus and tropic groups were made according to criteria established by Yeates et al (13). A taxon and trophic group diversity index was estimated via the Shannon Diversity Index (H) where: $H = \exp(-\Sigma P_i(\ln P_i)$ when P_i is equal to the proportion of the genus or taxon "i" to the total population (14). H increases as diversity increases. Community maturity values were estimated as the Maturity Index (MI): $MI = (\Sigma V_i f_i)n$, when V_i = colonizer- persister value of taxon "i", f_i = frequency of taxon "i" in the sample, and n = total nematode population density(15). The MI scale is 1 to 5, reflecting colonizers and persisters, respectively.

RESULTS AND DISCUSSION

SOIL CHEMICAL ANALYSIS

The soil chemical analysis (Table 1) shows that for most levels of the plots, there is little residual petroleum contamination. A noteworthy exception to this is the surface level of the Oil plot. In both the GC and IR analysis, the TPH values reflect a continued petroleum presence particularly near the surface. Although there are traces of contamination still in the OF plot, these concentrations are extremely low in comparison to those of the O plot for the same level.

For the C plot, the current TPH values are below detectable concentrations (10 and 25 ppm for IR and GC, respectively). The soil was known to be uncontaminated before the time of the 1992 study and was not sprayed with the contaminating crude oil during the study (5).

In all levels of all three plots, nitrate values were similar and below 1.0 ppm. The levels of ammonium, however, show differences between the plots. The Control Plot had the lowest levels, ranging from 3.1 to 8.1. The Oil Plot had values ranging from 8.3 to 10.6 while the Oil and Fertilizer Plot possessed the highest levels, ranging from 12.9 to 14.7. There was no pattern for ammonium levels in regards to the depth of the sample within the plot.

Not surprisingly, the levels of nitrate are consistently lower than those of ammonium due to the fact that nitrate has a higher mobility rate in soil than ammonium (16). In addition, ammonium typically accumulates in areas of plant matter thus correlating with the overall higher levels in

comparison to nitrate as well as the high levels in the OF plot (which contained the highest plant biomass) in comparison to the other two plots (17).

PLANT ANALYSIS

A study of the indigenous plant species diversity was performed as well as a total plant biomass analysis because the differences between the plots at the time of sampling was quite obvious and striking. The similarity in productivity between the C and OF plots was noteworthy, having 3.1 and 3.4 kg of dry biomass respectively (comprising 37 and 41 percent of the total biomass of all three sites). It can be concluded that the removal of toxic hydrocarbons has returned the ability to support plant life to the OF plot. This is in contrast to the continued presence of high levels of hydrocarbons in the O plot and the low quantities of plants growing on the area (1.2 kg, or 22% of the total dry biomass).

In regards to the plant species diversity found on the plots (Table 2), the low diversity of the O plot is attributed to residual soil toxicity as supported by both the soil chemical analysis and Microtox ^{R} data. The C plot, never having been contaminated, was expected and found to have a wide diversity of plant life present. The OF plot was found to have a relatively wide range of plants present and this was again attributed to the more complete removal of the toxic contaminants and resulting return to a condition suitable for plant habitation. Despite this apparent recovery, however, many of the plant species found still reflect a disturbed site.

The residual effect of the addition of fertilizer to the OF plot is credited with the lower species diversity of the plot in comparison to that of the C plot (18). The addition of fertilizer has been found to increase the competitive growth of those plants which first colonize the area, inhibiting the growth of plants that would later establish themselves in the absence of any growth-stimulants although the actual chemical nutrients in the fertilizer have long since washed out of the soil. This explanation is strongly supported by work performed by Inouye and Tilman which observed vegetation similarity as a result of changing nitrogen levels over long time periods (18).

NEMATODE ANALYSIS

Total nematode densities were highest in the O plot, and 91% of the O plot's population was comprised of microvores (predators of bacteria and unicellular eucaryotes). The C and OF plots had significantly lower numbers of this trophic group. The Shannon Diversity Index (H) was lowest in the O plot (1.80) and may reflect residual

petroleum contamination in the plot. H was highest in the C plot (4. 69) and only slightly lower in the OF plot (3.85). Community Maturity Values (MI) were low in the OF plot (1.49) as an effect of the addition of fertilizer. The values for the C and O plots were higher than those for the OF plot (2.08 and 1.96, respectively) and similar to one another. These values tend to indicate a shift away from persisters and towards colonizers (14).

OVERALL SUMMARY

When comparing the C to the OF plot, nematode and Microtox^{R} studies do not correspond with residual petroleum contamination levels. However, when comparing the C to the O plot, plant biomass and diversity studies as well as toxicity analysis do reflect persistent petroleum hydrocarbons in the soil. Thus, fertilization may not only speed the removal of petroleum contamination, but also affect plant and nematode diversity by favoring early colonizers.

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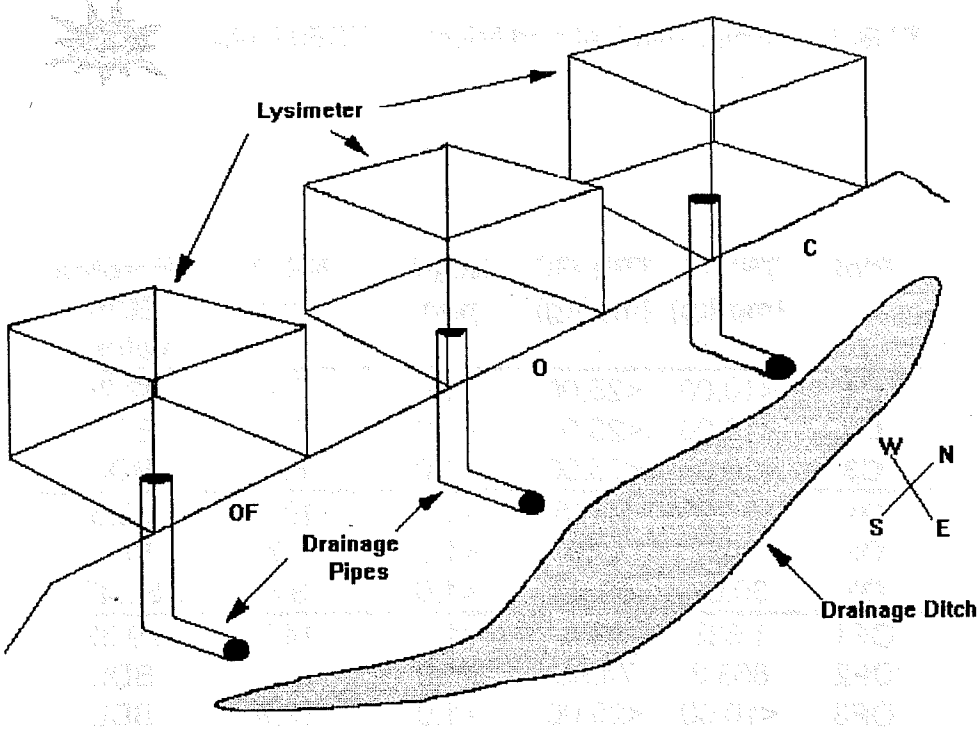

Figure 1: Schematic Diagram of Research Site

TABLE 1: Soil Chemical and Microtox EC50 Data

Plot	TPH-IR (mg/kg)	TPH-GC (mg/kg)	NO_3-N ppm	NH_4-N ppm	Microtox EC50 values
C1	<10.00	<25.00	<1.0	5.9	82.28
C2	<10.00	<25.00	<1.0	3.1	87.7
C3	<10.00	<25.00	<1.0	8.1	BDL
O1	16,299	5,365	<1.0	10.6	33.5
O2	1,452	249	<1.0	9.7	BDL
O3	30.67	59.97	<1.0	8.3	80.47
OF1	1,633	83.8	<1.0	14.7	79.83
OF2	863.3	74.95	<1.0	14.2	BDL
OF3	<10.00	<25.00	<1.0	12.9	BDL

BDL: Below Levels of Detection

Plots are abbreviated by plot name and level;

Example: C1 = surface level of the control plot

Table 2: Plant Species Identified on Each Plot

Control Plot:

Bromus sp.
Cirsium sp.
Croton sp.
grass sps.
Hieracium sp.
Krigia dandelion
Lepidium virgincum
Plantago aristata
Rudbeckia hertia
unidentifiable species (1)

Oil Plot:

Cirsium vulgare
grass sps.
Krigia dandelion

Oil and Fertilized Plot:

Andropogon scoparius
Aristida oligantha
Chenopodium album
Echinochloa crusgalli
Sorghum halapense
unidentifiable species (1)

In addition to these species, the following were found on all three of the plots:

Conyza canadensis
Oxalis stricta
Pyrrhopapus carolinianus

Characterization of Confined LNAPL

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Standard site characterization strategies utilized at sites contaminated by free phased Light Non-Aqueous Phased Liquids (LNAPL) have proven ineffective at determining the nature and extent of the free phased LNAPL contamination where it exists in confined conditions. Common site characterization strategies involve drilling to the first water encountered, usually the water table, and installing wells to monitor the free phased LNAPL that is expected to "float" on the water table. However, if the free phased LNAPL is confined within a deeper permeable zone, the LNAPL will not be detected with the standard "first water" characterization strategy.

LNAPL is not commonly expected in confined conditions because the buoyancy of the LNAPL typically does not allow it to penetrate into the saturated zone. At a site in the Texas panhandle, LNAPL was encountered in confined conditions in a 10 foot thick, fractured dolomite overlain by an impermeable claystone. The LNAPL appears to be from a past pipeline leak which occurred in the vicinity of the shallow subcrop of the dolomite. The dolomite exhibits fairly high relief, dipping steeply from the shallow subcrop into a synclinal axis at a depth of 110 feet below ground surface. The LNAPL is believed to have entered the more permeable dolomite and migrated down dip through the vadose zone in the dolomite. At the water table in the dolomite, the buoyancy of the LNAPL prevented it from further down dip migration. As the LNAPL accumulated on the water table in the permeable dolomite, the pressure of the LNAPL column increased sufficiently to exceed the hydrostatic pressure in the aquifer allowing the LNAPL to continue to migrate down dip below the water table into confined conditions. LNAPL is currently 1500 feet from the former pipeline leak and has a maximum measured

thickness in one well of over 60 feet. At this location, the LNAPL has risen over 50 feet above the top of the permeable dolomite in a monitoring well.

At this site, the "first water" characterization strategy delineated a limited extent of free phased LNAPL on the water table. Based on this characterization, an LNAPL recovery system was installed to address the shallow LNAPL. Subsequent characterizations conducted at the site have detected the deeper more extensive LNAPL in confined conditions. These characterizations have fully defined the permeable dolomite and the confined LNAPL allowing for remedial activities to be directed at the full extent of LNAPL contamination. Although this site is somewhat unique, a second site has been identified in the area with similar confined LNAPL. These sites demonstrate the need for a full characterization of an LNAPL contaminated site. When investigating similar sites, one should at least be aware of the possibility of conditions that could cause LNAPL to be present in confined conditions.

INTRODUCTION

Characterization of numerous sites, where Light Non Aqueous Phase Liquids (LNAPLs) have been released from petroleum storage tanks and pipelines, have resulted in an understanding of the behavior of the LNAPL in both the soil and groundwater. This understanding has led to a standard characterization approach for determining the nature and extent of LNAPL in the subsurface at LNAPL release sites. The standard characterization approach focuses on the interface between the vadose zone and the saturated zone because the buoyant nature of LNAPL results in a floating LNAPL "pool" on the groundwater table. At two sites in the Texas panhandle, LNAPL has been encountered in confined conditions below the interface between the vadose zone and the saturated zone. Characterization of one of these sites using the standard approach proved to be ineffective at defining the nature and extent of LNAPL and resulted in the installation of a recovery system at the site that was inable to collect LNAPL from the entire plume. A complete understanding of the site hydrogeology, the spill history and the contaminant flow pathways prior to the installation of the remediation system, would have avoided unnecessary costs and time.

STANDARD LNAPL CHARACTERIZATION

The standard characterization approach for LNAPL contaminated sites has been developed based on the understanding of the behavior of the LNAPL in the subsurface (1,2). Generally, the LNAPL is released from a storage tank or pipeline and migrates through the vadose zone to the water table (Figure 1). At the water table, the buoyancy

of the "lighter-than-water" LNAPL restricts its downward migration and causes the LNAPL to spread out on the water table. The LNAPL forms a "pool" or "pancake" of free hydrocarbon which floats on the water table. Although the simple pancake model is complicated by hetergenities in the lithology (3), water level fluctuations (4), and the fluid properties of the LNAPL, the free phased LNAPL is still concentrated at, or near, the vadose zone-water table interface. The presence of this "pool" on the water table has resulted in the focus of most investigations at LNAPL sites to be on the interface between the vadose zone and the water table. Investigations commonly include obtaining soil samples through the vadose zone to the water table and then installing a monitoring well with the screen interval straddling the interface (Figure 1). Water and LNAPL measurements can then be obtained from the monitoring well in addition to obtaining a water sample. Because the LNAPL "pool" is believed to be present only on the water table, this approach allows for the determination of the volume of free LNAPL "floating" on the water table and the determination of the highest concentration of organic contaminants dissolved in the groundwater. Based on this characterization approach, if no organic contamination is detected in these shallow water table wells the investigation would be terminated. At relatively simple sites where the subsurface geology is primarily composed of homogenous sand with uniform porosity and permeability, the general concept of floating LNAPL present on the water table is adequate (Figure 1).

CONFINED LNAPL DEFINITION

Based on the standard concepts of LNAPL behavior in the subsurface, LNAPL would not be expected to be present below the interface between the vadose zone and the water table. However, under certain geological conditions LNAPL has been encountered below the water table in confined conditions. Confined LNAPL is defined as LNAPL present within a permeable zone in the subsurface under a sufficient pressure, such that, when it is penetrated by a borehole, or well, the LNAPL rises above the top of the permeable zone or the level at which it was encountered during drilling (Figure 2). The presence of LNAPL in confined conditions can only occur when a sufficient volume of LNAPL has been released to the subsurface and allowed to accumulate in a stratigraphically restricted permeable zone below the water table. The accumulation of LNAPL must generate a sufficient pressure to overcome the bouancy pressure, the hydrostatic pressure, and the entry pressure of the permeable zone. As this pressure increases the LNAPL can move further below the water table and into confined conditions (Figure 3). Penetration of the permeable zone with a borehole will cause the confined LNAPL to rise above the top of the permeable zone. The downward migration of the LNAPL can result in the LNAPL being present beneath an unimpacted water table groundwater system.

CONFINED LNAPL CASE STUDY

At the site of a historic petroleum pipeline release in the Texas panhandle, confined LNAPL was encountered after several phases of characterization and after a remediation system was installed to address the shallow water table contamination. The LNAPL release was originally identified when a kerosene/diesel hydrocarbon was detected in a groundwater well. Skimmer pumps were installed in the well and an investigation initiated. Three phases of investigation, including a total of 11 soil borings and 17 monitoring wells, were conducted focusing on the shallow vadose zone-water table interface. Based on the soil borings and the wells, the shallow geological conditions were interpreted to consist of a permeable sand overlying interbedded impermeable claystones. A water table system was encountered in the permeable sand and in fractures in the claystones. A permeable dolomite was present beneath the claystone which contained a confined water system. During the initial characterizations, care was taken not to penetrate the permeable dolomite because the water in this system was not believed to be impacted. The water system in the permeable dolomite was confined and the upward gradient was thought to restrict the downward migration of the lighter-than-water LNAPL. All of the soil borings terminated at the water table and the wells straddled the water table.

The extent of the LNAPL plume was defined in the shallow sand and fractures in the claystone (Figure 4). Based on the definition of the LNAPL plume, a remediation system was installed to address this shallow contamination. Subsequent to the installation of the shallow remediation system, a downgradient well was installed at a location where the shallow sand and claystone were thin and in an area that did not contain shallow LNAPL. The well penetrated the permeable dolomite and LNAPL was encountered. This discovery spurred two additional investigations designed to establish the extent of free LNAPL in the deeper dolomite zone.

The additional investigations focused on understanding the distribution and aquifer properties of the permeable dolomite and the extent of the free LNAPL in the dolomite. The dolomite at the site displays relatively high relief, dipping steeply from a shallow subcrop on the west side of the site through a deep synclinal axis and rising again to the surface on the east side of the site. The dolomite also crops out in both a north and south direction in deeply eroded stream channels. The permeability of the dolomite (10X10-2 cm/sec) is significantly more permeable than the surrounding claystones (10X10-6 cm/sec). Both the increased permeability in the dolomite and the structural relief on the dolomite provide controls on the distribution of the free LNAPL. The distribution of confined LNAPL in the dolomite is more extensive than the shallow LNAPL. The confined LNAPL has migrated significantly further from the old source area than the shallow LNAPL (Figure 4).

At this site, the LNAPL appears to have been released from a pipeline in the vicinity of the subcrop of the permeable dolomite (Figure 5). At this location, the overlying sand is thin and the claystone has been eroded placing the dolomite close to the surface. The LNAPL

gravity drained through the vadose zone in the overlying sand and into the vadose zone of the permeable dolomite. The LNAPL continued down dip in the permeable dolomite to the water table. At this depth, the LNAPL could not migrate further due to the buoyancy restricting its downward migration and the permeability restrictions of the impermeable claystones above and below the permeable dolomite. The LNAPL accumulated on the water table and this accumulation increased the LNAPL pressure sufficiently to overcome the buoyancy and the hydrostatic pressure. The LNAPL was then able to continue its down dip migration into confined conditions. Eastward migration of the LNAPL was restricted by the steep east limb of the syncline and the claystone-cored anticline to the east (Figure 5). The LNAPL migrated in a northerly direction and has stablized in its current location.

Currently, the confined LNAPL is being collected from the existing monitoring wells containing a significant volume of LNAPL. A total of over 500 gallons of LNAPL have been recovered from the dolomite. Monitoring wells are located and monitored to ensure that LNAPL does not migrate in any direction.

CHARACTERIZATION OF CONFINED LNAPL

The presence of confined LNAPL is a fairly unique condition and is not present at most LNAPL contaminated sites. However, should certain conditions exist the characterization strategy should consider the potential for confined LNAPL and include identification of the extent of the confined LNAPL. The potential for confined LNAPL is based on two site conditions: the site hydrogeology and the site spill history. A complete understanding of each of these conditions allows for the evaluation of the potential for confined LNAPL.

The hydrogeological conditions required for confined LNAPL to exist at a site include 1) alternating permeable and impermeable zones, 2) structural relief and 3) a subcrop or outcrop of one of the permeable zone. These hydrogeological conditions are necessary because the deeper permeable zone must be confined by a less permeable zone above and below. The less permeable zone restricts the upward movement of groundwater and LNAPL. In addition, there must be a location for the LNAPL to enter the permeable zone. This entry point will be a subcrop or outcrop of the permeable zone. At this location the LNAPL can enter into the permeable zone and begin its downward migration. If neither of these conditions exist at a site, then LNAPL is not likely to be present in confined conditions.

The spill history required for confined LNAPL to be present at a site include a release of free LNAPL in the vicinity of the outcrop or subcrop of the permeable zone. The release must be in a position where the downward migration of the LNAPL can enter into the permeable zone. The release must also be of a sufficient volume to create enough

pressure for the LNAPL to enter the saturated zone and maintain a flow connection throughout the entire migration pathway.

If these conditions are present at an LNAPL site, then the characterization strategy should include a focus on the deeper permeable zones where LNAPL may be in confined conditions. The confined LNAPL characterization should include the following:

- Determine the extent of both the impermeable and the permeable zones at the site including the subcrop and/or outcrops of the different zones
- Determine the porosity and permeability characteristics of the different zones
- Determine the spill location and spill volume

This characterization should include detailed surficial field mapping, drilling soil borings and installing wells in both the shallow water table zones and in the deeper confined zones to fully understand the hydrogeolgical conditions at the site. Installation of deeper wells are expensive. However, this investigation expense will be offset by the increased efficiency of the required recovery system.

CONCLUSIONS

Current understanding of LNAPL contaminated sites has resulted in a standard approach to the characterization that focuses on the shallow water table. This approach is not effective at characterizing sites where LNAPL is contained in confined conditions. Although confined LNAPL is not expected at all LNAPL sites, it should be considered as a potential condition and included in the characterization approach. Sites with alternating permeable and impermeable zones, and a release in the vicinity of the subcrop or outcrop of a permeable zone should include an evaluation of potential confined LNAPL. The full characterization and identification of confined LNAPL will allow for the proper evaluation and installation of effective remediation strategies.

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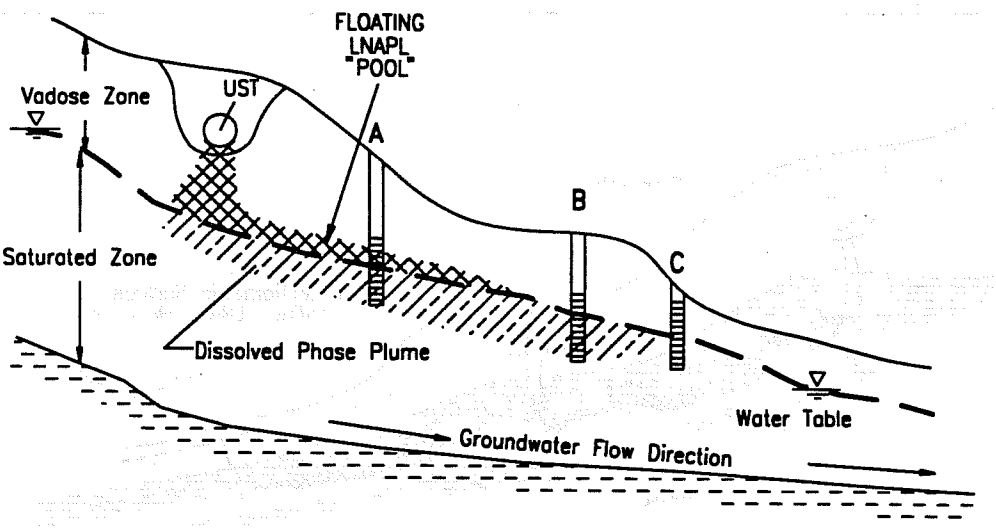

Figure 1. Schematic Cross Section of Traditional Characterization Approach

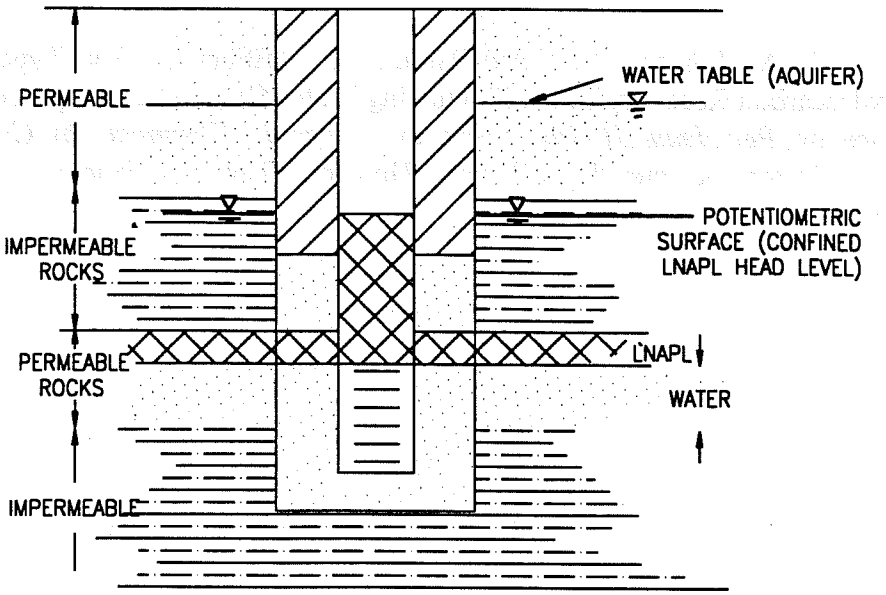

Figure 2. Confined LNAPL in a Well

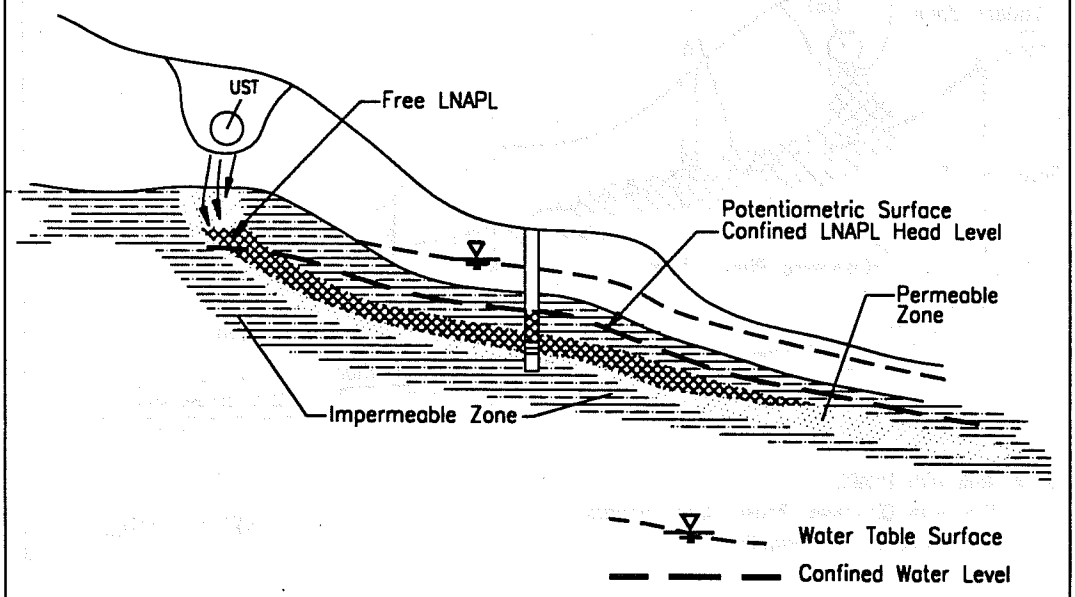

Figure 3. Schematic Cross Section of Confined LNAPL

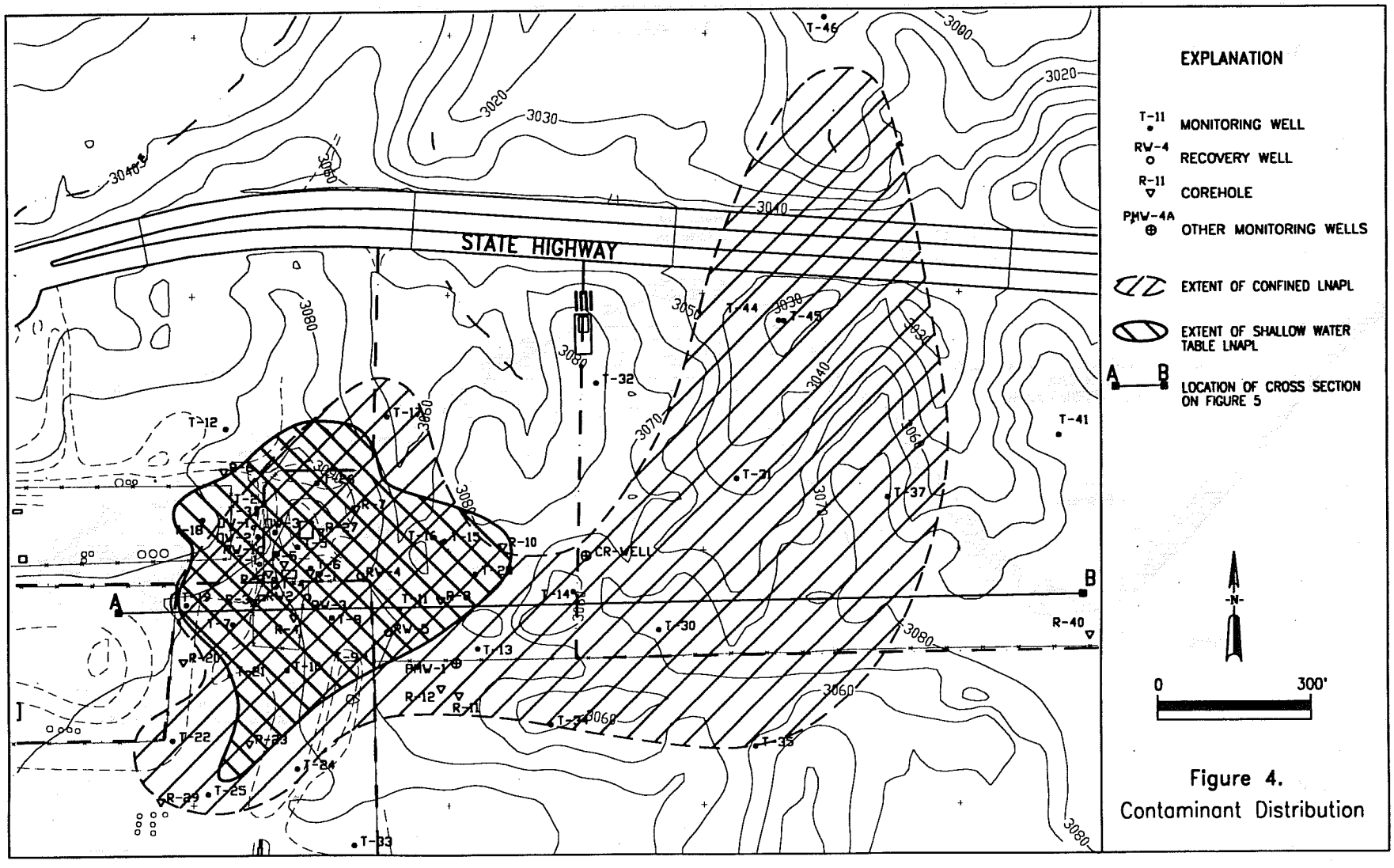

Figure 4.
Contaminant Distribution

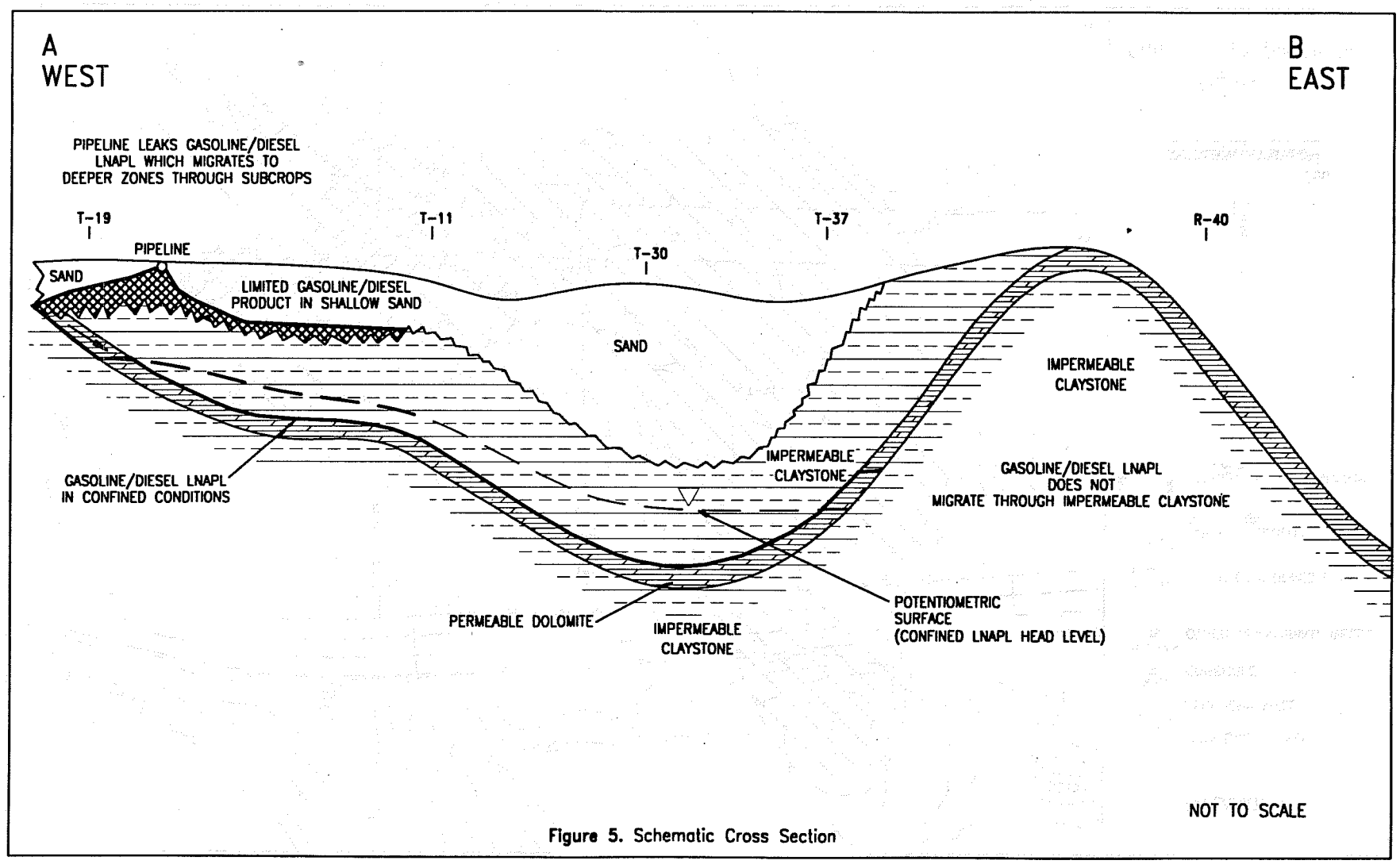

Figure 5. Schematic Cross Section

Demonstration of Natural Attenuation Through Isotope Analysis

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Biological degradation is believed to be the mechanism of natural attenuation for removal of petroleum hydrocarbons from an aquifer. Most organic compounds found in crude and refined petroleum hydrocarbon mixtures are known to degrade under aerobic and anaerobic conditions. Under aerobic conditions, dissolved oxygen is the electron acceptor used by the microorganisms to degrade petroleum hydrocarbons. Under anaerobic conditions, sulfate, ferric iron, and nitrate are known alternative terminal electron acceptors. Concentration levels of these electron acceptors in a contaminated ground water plume have been widely used as evidence for the occurrence of natural attenuation. However, due to possible localized variations in geochemical deposition, concentration levels of sulfate and nitrate were often found to be inconsistent. Meanwhile, the isotope ratio of sulfate and nitrate are much more uniformly distributed. Biological oxidation and reduction of these geochemicals leaves distinctive signatures that are unaffected by concentration variation. Isotope analysis of these components allows us to determine observed concentration variations due redox process in biodegradation rather than local variation in groundwater composition. The isotope ratio also provides quantitative information on the extent of oxidation-reduction reaction. As a result, the isotope ratio provides a more reliable indication of natural attenuation then concentration data alone Examples of the application of isotope analysis are illustrated in a case study at Guadalupe Oil Field. The stable isotope ratios of nitrogen ($\delta^{15}N$) in dissolved nitrate have provided evidence for the occurrence and the mechanism for anaerobic degradation in ground water. The stable isotope ratios of sulfur ($\delta^{34}S$) in dissolved sulfate not only provided an additional evidence for the occurrence of intrinsic bioremediation, but also gave quantitative information on sulfate reduction based on the degree of sulfur isotopic fractionation. The sulfur isotope data also help to explain an observed sulfate concentration anomaly in ground water.

INTRODUCTION

Remediation by natural attenuation is an approach by which a contamination is reduced and removed by natural processes without active human intervention. The processes involved can be physical (dispersion and volatilization), chemical (adsorption and reactions), or biological (aerobic and anaerobic degradation). For petroleum hydrocarbons, biodegradation is the primary mechanism for the mass removal (1-3). Therefore, natural attenuation is also referred to as bioattenuation or intrinsic bioremediation.

Most organic compounds found in crude and refined petroleum hydrocarbon mixtures are biologically degradable under both aerobic and anaerobic conditions. Under aerobic conditions, dissolved oxygen is the electron acceptor used by the microorganisms to degrade petroleum hydrocarbons (4). Under anaerobic conditions, nitrate, ferric iron, and sulfate have been found to be the terminal electron acceptors in biodegradation of petroleum hydrocarbons (5-8). Assuming uniform background levels in soil and groundwater, changes in concentrations of various electron acceptors (dissolved oxygen, nitrate, sulfate, etc.) and metabolic byproducts (carbon dioxide, ferrous iron, methane, etc.) are widely used as evidence for natural attenuation (9-11).

Assumption of uniform background levels for constituents dissolved in flowing groundwater is intuitively sound for small areas where diffusion and dispersion will tend to smooth out any local variation in concentration over time. However, this assumption doesn't always hold true for a large site, as we found out at Guadalupe Oil Field. Fortunately, there are other well established techniques available (e. g. stable isotope analysis) for "fingerprinting" biological processes that don't rely on uniform background concentrations of the dissolved electron acceptors. Three of the components used to quantitatively evaluate natural attenuation (11) have stable isotope ratio signatures that can be used to supplement the interpretation of concentration data alone. These components include the electron acceptors sulfate and nitrate, which are utilized in the oxidation of hydrocarbons, and methane, which may be generated as part of biodegradation process under anaerobic conditions.

The stable isotope ratio ($^{34}S/^{32}S$ or $\delta^{34}S$ ‰) of sulfur in dissolved sulfate, for example, can provide an additional evidence for the occurrence of intrinsic bioremediation using sulfate as an electron acceptor (sulfate reduction). Sulfate reduction may be assimilatory or dissimilatory in the nature. Assimilatory sulfate reduction, which occurs in plants and animals, results in only slight isotope fractionation and the isotope ratio of residual sulfate will only be slightly altered as sulfate is removed. In contrast, dissimilatory reduction, which occurs in the

anaerobic bacterial reduction of sulfate and oxidation of organic matter such as petroleum hydrocarbons, results relatively large isotope fractionation (12). As a result, the isotope ratio of the dissolved sulfate is significantly altered as sulfate is reduced. Based on the degree of sulfur isotopic fractionation, the extent of sulfate reduction can be estimated from the analysis of the isotope ratio of the remaining sulfate dissolved in the water.

When nitrate is used as the electron acceptor in the oxidation of organic matter (denitrification), then the stable isotope ratio ($^{15}N/^{14}N$ or $\delta^{15}N$ ‰) of the nitrate is significantly altered as a consequence of isotope fractionation (13). Similar to sulfate, the degree of denitrification in the groundwater can be estimated from the analysis of the isotope ratio of the remaining nitrate dissolved in the water.

Biogenic methane is commonly associated with anoxic aqueous environments, including petroleum hydrocarbon plumes in ground water. There are two biogenic pathways for methane generation: CO_2 reduction and acetate fermentation. These two pathways can be distinguished on the basis of carbon ($^{13}C/^{12}C$) and hydrogen (D/H) stable isotope ratios (14). For methane in anoxic groundwater, stable isotope studies show that methane has D/H ratios (> 250 ‰) characteristic of the CO_2 reduction pathway (15). In contrast, methane generated during hydrocarbon degradation has D/H ratios (< 250 ‰) characteristic of acetate fermentation (16,17). Thermogenic methane derived from natural seeps have D/H ratios in the same range as methane formed from CO_2 reduction. Therefore, D/H isotope ratio for methane less than 250 ‰ in flowing groundwater can be considered indicative of natural attenuation of petroleum hydrocarbons.

In this paper, examples of the application of isotope analysis will be illustrated in a case study at Guadalupe Oil Field. For this study, the stable isotope ratio data for sulfate and nitrate will be used to demonstrate loss of each of these electron acceptors due to bioremediation of hydrocarbons in the groundwater. At this site, the methane content in the groundwater was too low to collect samples for stable isotope ratio determination. In another part of the field, however, methane was collected in the soil gas immediately above the groundwater. Natural remediation of methane in unsaturated zone will be shown to be identified by isotopic fractionation of the methane.

METHODS

Guadalupe Oil Field is situated in a hilly coastal region of Central California. A hydrocarbon plume around one of the abandonment oil production wells is defined by 10 monitoring wells (MW-1 to MW-10 in **Figure 1**). Petroleum hydrocarbon free product in diesel range was found in a monitoring well

(MW-1) near the center of the hydrocarbon plume. Based on the potentiometric surface determined on May 1995 (**Figure 1a**), the ground water is flowing in the north west direction. Relative to the plume position, MW-3 is situated upgradient, MW-1 and MW-2 near the center, and four wells downgradient. A new monitoring well (MW-11, not shown in Figure 1) was recently installed half way between MW-1 and MW-6, a downgradient well. An additional monitoring well (MW-12, also not shown) approximately 1000 feet upgradient of MW-3 was also sampled to determine the background condition upgradient. At the site, the average depth to ground water is approximately 100 feet.

Ground water dissolved oxygen was measured in the field using a dissolved oxygen meter in a flow-through cell to avoid aeration of the ground water sample (11). Dissolved oxygen readings were continuously monitored during purging of the well until the readings reached a steady state. Following well purging, ground water samples were collected for field and laboratory analysis. Field analysis of nitrate, sulfate, and ferrous iron were made on site immediately following the sample collection using analytical field kits. Laboratory analysis include benzene, toluene, ethyl-benzene, and xylenes (BTEX) and total petroleum hydrocarbons (TPH). Stable isotope analysis for sulfur ($\delta^{34}S$ $^{o}/_{oo}$) from sulfate and nitrogen ($\delta^{15}N$ $^{o}/_{oo}$) from nitrate were also performed for selected wells.

RESULTS

Historical ground water data from the site are very limited. The ground water TPH data from two available sampling events are graphically presented in **Figures 1a** and **1b**. Because of the lack of long term TPH data, the reduction of total hydrocarbon concentrations observed may be attributed to either a seasonal variation or intrinsic bioremediation. Measurements of various electron acceptors (dissolved oxygen, nitrate and sulfate) and a metabolic byproduct (ferrous iron) were made for additional evidence of natural attenuation (**Table 1**).

The dissolved oxygen measurements indicated that the ground water down gradient of the hydrocarbon plume was in aerobic conditions, and the ground water within the plume was at or near anaerobic conditions, both of which are not unexpected. However, the ground water from MW-3 and MW-12 upgradient of the plume was also found to be in a near anaerobic state. Because of the presence of a known hydrocarbon plume about 3000 feet upgradient, it is possible that all the dissolved oxygen in the ground water upgradient has already been biologically consumed.

No clean correlation between nitrate and TPH concentration exists. Nitrate was found to be depleted in some of the clean background wells (MW-4, MW-5, and MW-7). Some of the low nitrate readings in the upgradient side of the plume

are consistent with the anaerobic conditions suggested by the low dissolved oxygen concentration (MW-5, MW-7). However, some nitrate readings are inconsistent with dissolved oxygen distribution (MW-3, MW-4, MW-10). The inconsistencies can be due to different sampling events (for dissolved oxygen in October vs. nitrates in December), or local variation in nitrate concentration. Unlike oxygen or sulfate, we believe that the sources for nitrate are more localized, resulting from plants, animals, and human activities.

The sulfate and ferrous iron distributions are generally consistent with each other, *i.e.*, the low sulfate and high ferrous iron concentrations are in the same well (**Table 1**). The only exception is the sulfate measurement in MW-7 well, where sulfate concentration is 3-4 times of those found in all the other wells. The ferrous iron and sulfate concentration contours without the sulfate value from MW-7 (**Figure 1c** and **1d**) are in general agreement with the plume geometry (**Figures 2a** and **1b**), where the sulfate valley and ferrous peak match the TPH concentration peak. The low sulfate and high ferrous iron concentrations within the hydrocarbon plume are also consistent with low dissolved oxygen readings, which suggests anaerobic biodegradation mechanisms within the plume. The extremely low sulfate concentration and high ferrous iron concentration in MW-2 suggest a highly extensive anaerobic biodegradation process using SO_4^{2-} and Fe^{3+} as terminal electron acceptors in the center of the hydrocarbon plume. The ground water values of low sulfate and high ferrous iron are evidence of the occurrence of intrinsic bioremediation in Guadalupe Oil Field.

ISOTOPE ANALYSIS

Stable isotope analyses for sulfur in sulfate and nitrogen in nitrate were made for ground water from selected wells: MW-3 (upgradient), MW-2 (beneath plume) and MW-8 (downgradient). The sulfate concentration data for the initial (field) and later (lab) sample collections are listed in Table 2. Because of the high anomaly in the sulfate concentration in ground water for MW-7, it is also included in the sulfur isotope analysis. Although the magnitude of sulfate concentration may differ between the field and lab analysis due the different sample treatments, trends of both analyses are similar (**Table 2**). The sulfate concentration in MW-7 is much higher than that in the other wells for both laboratory and field analyses.

A background $\delta^{34}S$ ratio of 6.4-6.5 ‰ was found in wells upgradient (MW-3) and outside (MW-7) the hydrocarbon plume, even though the two wells have shown different ground water sulfate concentrations (**Table 2**). The background $\delta^{34}S$ ratio of 6.5 ‰ is in the range of typically sulfur isotope ratio for sulfate found in rain water (12). Whereas a higher sulfur isotope ratio was found beneath (24.3 ‰ in MW-2) and downgradient to the plume (15.2 ‰ in MW-8), where isotope fractionation is believed to be caused by anaerobic bacterial

reduction of sulfate in the ground water (19). Based on the degree of sulfur isotopic fractionation (12), the extent of sulfate reduction is estimated to be approximately 50% beneath the plume (MW-2), and 30% downgradient of the plume (MW-8). Therefore, stable sulfur isotope ratio ($\delta^{34}S$ ‰) data provide an additional evidence for the occurrence of intrinsic bioremediation using sulfate as an electron acceptor in the ground water at Guadalupe Oil Field.

The background stable isotope ratio of nitrogen ($\delta^{15}N$) for nitrate in ground water is believed to be near the ratio of nitrogen in the air, which is at 0 ‰. The slight positive nitrogen fractionation (3 ‰) for nitrate in the upgradient well MW-3 (Table 2) suggests some utilization of nitrate biologically as electron acceptor (20), which is consistent with the observed anaerobic condition in MW-3 (Table 1). Nitrate utilization in MW-2 appears to be complete with no measurable amount of nitrate and a part per million level of dissolved ammonia in the ground water. Because of insufficient amount of nitrate, measurement of nitrogen isotope ratio was not made for MW-2. A highly positive isotope ratio ($\delta^{15}N$) of 7.6 ‰ for MW-11 immediate downgradient from the center of the hydrocarbon plume near MW-1 and MW-2 suggests extensive microbial denitrification as in an anaerobic biodegradation of hydrocarbons (20). A slight negative isotope ratio ($\delta^{15}N$) of -1.3 ‰ for MW-8 further downgradient from the plume indicates a possible nitrification process from ammonia to nitrate, that leads to negative nitrogen isotope fractionation for nitrate (21), which is consistent with the observed aerobic condition in MW-8.

CONCLUSIONS

Application of isotope analysis techniques can help demonstrate and quantify intrinsic bioremediation processes. Stable isotope ratio signatures for alternative electron acceptors such as sulfate and nitrate can be used to supplement the interpretation of concentration data. Examples of the application of isotope analysis are illustrated in a case study at Guadalupe Oil Field. The stable isotope ratios of nitrogen ($\delta^{15}N$) in dissolved nitrate have provided evidence for the occurrence and the mechanism for anaerobic degradation in ground water. The stable isotope ratios of sulfur ($\delta^{34}S$) in dissolved sulfate not only provided an additional evidence for the occurrence of intrinsic bioremediation using sulfate as an electron acceptor (sulfate reduction), but also gave quantitative information on sulfate reduction based on the degree of sulfur isotopic fractionation. The sulfur isotope data also help to explain an observed sulfate concentration anomaly in one of the ground water well.

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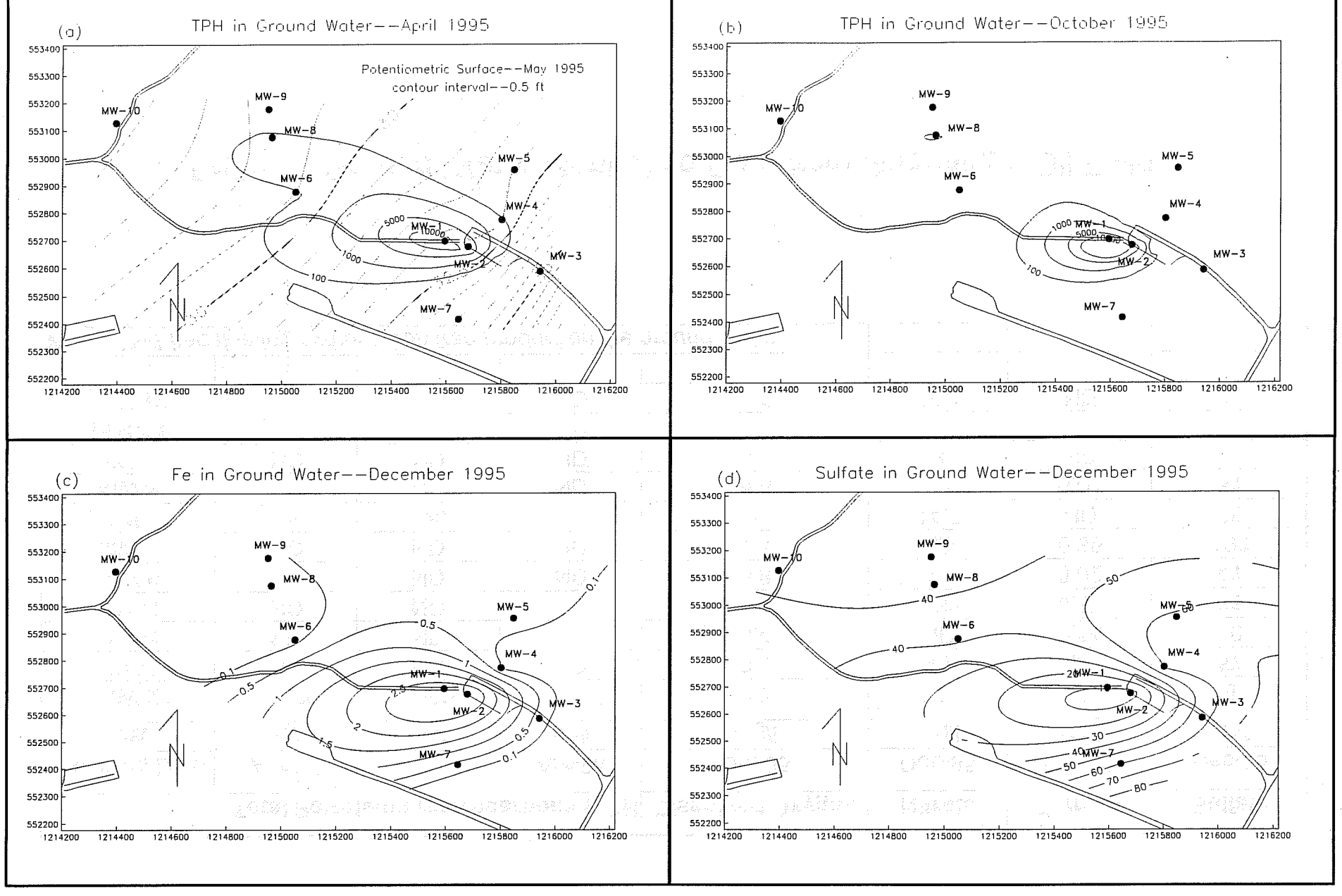

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Figure 1. TPH in ground water for J8 Area at Guadalupe Oil Field. Also plotted are ferrous iron (c) and sulfate (d) in ground water. All concentration units are ug/L. The potentiometric surface for May 1995 is included (a) to show ground water flow direction. The ticks and labels along each plot indicate dimensions in surveyed coordinates (ft).

	Total Petroleum Hydrocarbons (TPH			Dissolved Oxygen	Nitrate	Ferrous	Sulfate
Sampling Date	Apr-95	Oct-95	Apr-96	Oct-95	Dec-95	Dec-95	Dec-95
unit	µg/l	µg/l	µg/l	mg/l	mg/l	mg/l	mg/l
MW-2	10000	6900		0.7	ND	>3	8
MW-3	ND	ND	ND	0.3	9.7	0.31	57
MW-4	110	ND		5.4	ND	0.14	60
MW-5	ND	ND		0.6	1.32	0.37	61
MW-6	90	ND	ND	5.8	18	0.02	41
MW-7	ND	ND	ND	1.4	ND	0.39	196
MW-8	220	120		6	14.5	ND	38
MW-9	ND	ND	ND	6.8	22	0.01	31
MW-10	ND	ND	ND	6.2	3	ND	36
MW-11			ND				
MW-12	ND	ND	ND	0.5	14.1	ND	41
Well MW-1 had floating hydrocarbon free product on the ground water							

Table 1. Ground Water Monitoring Data from Guadalupe Oil Field

	Nitrate		^{15}N in Nitrate	Ammonia	Sulfate		^{34}S in Sulfate
Sampling Date	Dec-95	Jul-96	Jul-96	Jul-96	Dec-95	Dec-95	Dec-95
Method	Field	Lab	Lab	Lab	Field	Lab	Lab
unit	mg/l	mg/l	$\delta^{15}N$ °/oo	mg/l	mg/l	mg/l	$\delta^{34}S$ °/oo
MW-2	ND	<0.2		1.659	8	8.2	24.3
MW-3	9.7	12.6	3	<0.006	57	12	6.5
MW-7	ND				196	21.9	6.4
MW-8	14.5	17.1	-1.3	<0.006	38	13.1	15.2
MW-11		16.9	7.6	<0.006			

Table 2. Stable Isotope Analysis for Guadalupe Oil Field

LEAD ISOTOPES AND HYDROCARBON REMEDIATION: FROM AGE-DATING TO VERIFICATION OF BIOREMEDIATION

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Site remediation, cleanup, and cost-recovery require answers to questions concerning the age and origins of hydrocarbon contamination as well as the effectiveness of remediation efforts. Lead isotope ratio analyses of refined products and impacted soils can be used independently and/or integrated with other biogeochemical data to help resolve these issues.

Systematic variations in lead isotope ratios of gasoline additives have been calibrated to produce a chronologic model capable of dating the time of a gasoline release with higher precision than previously possible (ALAS Model; Anthropogenic Lead ArchaeoStratigraphy). In the era of unleaded (e.g. low lead) gasolines, lead isotopes can be used to discriminate among different manufacturers' products as long as the crude oils used in the refining process differ.

Representative case histories are discussed which exemplify the application of lead isotopes and the ALAS Model to fingerprinting and age-dating gasoline releases. These investigations further demonstrate the method's effectiveness on both free product and soil matrices.

Current investigations in which lead and carbon isotopes are integrated to evaluate the time and extent of intrinsic bioremediation are briefly discussed. Our long-term goals are to better understand processes associated with intrinsic bioremediation and constrain the time scales of hydrocarbon degradation in the environment.

INTRODUCTION

Significant advances have been made over the last twenty-five years to eliminate lead (Pb) from gasoline, paint, and other products because of the inherent toxicity of this element. The issue of global lead pollution was initially brought to our attention through the efforts of Clair C. Patterson (Emeritus Professor of Geochemistry, California Institute of Technology) and his colleagues who demonstrated the ability of gasoline-derived lead to be retained in soils for decades, serving as a geochemical tracer of anthropogenic lead pollution (1-3). This relative immobility of lead in the environment, coupled with high precision lead isotope ratios (e.g. $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$), allows anthropogenic sources of lead to be fingeprinted and, in the case of leaded fuels, age-dated using a novel application of lead isotope ratio analyses.

Determining the time frame and source(s) of gasoline spills have far-reaching implications in site remediation, cleanup, and cost-recovery operations. Who is responsible for the contamination (identification of the PRP's, i.e. Potentially Responsible Parites)? When did the spill occur? Who is going to pay the cost of the cleanup? Such questions cannot be answered using standardized EPA protocols designed to identify the nature and probable extent of the contaminant(s) rather than the source(s). However, by expanding upon and refining the work initiated by Patterson, it is now possible to: (1) constrain the time of gasoline spills using calibrated changes in gasoline lead isotope ratios over time (ALAS Model; Anthropogenic Lead ArchaeoStratigraphy); (2) discriminate among sources of "unleaded" fuels (e.g. ppb levels of lead inherited from crude oils); and (3) integrate lead isotopic studies with other biogeochemical parameters to evaluate remediation efforts.

HISTORIC CHANGES IN GASOLINE LEAD ISOTOPE RATIOS

With the exception of ^{204}Pb, a stable isotope which is not a product of radioactive decay, the other three naturally-occurring isotopes of lead are daughter products of either uranium (^{206}Pb, ^{207}Pb) or thorium (^{208}Pb) decay. Like ^{204}Pb, they are stable, but are also said to be radiogenic because of their production through radioactive decay. As a result, ore lead isotope ratios increase over time as functions of the geologic age, crustal history, and U/Th concentrations of the host ore body.

Prior to 1968, < 10% of U.S. industrial lead (including lead for gasolines) originated from Mississippi Valley sources. Between 1968 and the late 1980's, this proportion increased systematically to over 80% (4). Given the anomalously high, radiogenic lead isotope ratios of Mississippi Valley ores

relative to those of other global sources (e.g. $^{206}Pb/^{207}Pb > 1.3$ versus 1.0-1.2 respectively), isotope ratios of the gasoline-derived, anthropogenic lead component in soils would be expected to become progressively more radiogenic during this time interval. Analyses of well-dated marine sediments collected near major oil refineries in Los Angeles, California substantiated this cause-effect relationship; anthropogenic $^{206}Pb/^{207}Pb$ ratios increased from 1.16 in 1966 to 1.18 by 1975 (1). Subsequent investigations by Patterson and others (5-8) demonstrated this trend continued through the 1980's, with $^{206}Pb/^{207}Pb$ ratios of gasoline-derived soil and atmospheric components reaching values of 1.22.

It became apparent, that time and source dependent changes in gasoline lead isotope ratios could produce a forensic chronologic tool to model ages of gasoline spills. However, questions concerning the availability of accurately-dated samples, nature of matrices (e.g. free products, soils, waters), ranges in gasoline lead additive isotope ratios (well constrained or scattered), geographic applicability, and model age resolution needed to be addressed.

DEVELOPMENT OF THE ALAS MODEL

MODEL CALIBRATION

Obtaining samples with well-defined ages is the foundation of any time-calibration curve. Marine sediment samples from Patterson's collection, received in the mid-1980's for another investigation, were augmented with samples provided by Oregon State University scientists (C. Huh and colleagues). Archived, refined gasolines of known age were obtained from the petroleum industry. Soil samples taken from sites impacted by well-documented gasoline spills were either provided by geotechnical firms or available from our own investigations. Age-dating techniques, providing uncertainties of < 1 year for ALAS calibration samples, included: real time sampling; documented records; labelled, archived samples; ^{210}Pb or ^{137}Cs ages; and varve chronology.

ULTRACLEAN CHEMISTRY AND HIGH PRECISION MASS SPECTROMETRY

The global nature of lead pollution requires all sample chemistry to be performed in an ultraclean laboratory using multiply distilled reagents with total process lead blanks maintained in the tens of picogram range or lower. Labware must be ultrapure quartz or TFE/PFA teflon which has been cleaned for two to six months prior to use. Stringent requirements were established to

insure accurate results are obtained on 20 - 50 nanograms of lead in samples (e.g. waters, low lead gasolines, hydrocarbons).

The development of new or modified EPA-type extraction techniques was required to extract anthropogenic lead from soil matrices. Sequential extractions with different solvents are often performed to evaluate the existence of multiple anthropogenic sources and identify natural background lead in soils. Liquid samples have typically been treated as a "whole" sample rather than an extract. However, compound-specific aqueous extractions are now employed to correlate dissolved phases with specific hydrocarbon plumes.

Lead isotope ratios are measured on a thermal ionization mass spectrometer (TIMS) and normalized to isotope standards available from what is now NIST (formerly NBS; most isotopic standards retain their NBS codes, such as NBS SRM 981, a common lead standard). Separation (fractionation) of lead isotopes does not occur in nature but does occur to levels of up to 0.1% per atomic mass unit in the TIMS. Hence, the normalization process involves frequent analyses of NBS lead isotopic standards to insure high precision and accurate lead isotope ratio analyses (typically 0.04% to 0.1% at the 95% confidence level).

LEAD ADDITIVES

Over the years, the United States has seen the rise and fall of numerous petroleum companies ranging in size from the "Mom and Pop" type to moderately-sized Independents to the Majors. By comparison, the number of firms selling gasoline lead additives were a rather small group. The Ethyl Corporation dominated, followed by Dupont which operated into 1985 and Nalco prior to 1984 (8). Discussions with former employees in the alkyllead industry indicate their sources of lead followed U.S. industrial lead market availability; i.e. Mississippi Valley sources increased through the 1970's into the 1980's. As a result, the characteristics of leaded gasolines during these years were: (1) lead isotope ratios became more radiogenic as the proportion of Mississippi Valley lead in alkylleads increased and (2) lead concentrations of additives "swamped out" the ppb-levels of natural lead inherited from crude oil sources.

GEOGRAPHIC APPLICABILITY

The ALAS Model evolved from a predecessor called the Los Angeles Borderland Industrial Lead Model (LABILE) which was designed to determine model ages of gasoline incursions in southern California. However, agreement

between ALAS Model ages based on published lead isotope ratios of well-dated gasoline-impacted sediment and urban aerosols (1-3, 5-10), suggested broader applications of the model throughout the United States. This conclusion has been supported by successful applications of the ALAS Model in California, Washington, Texas, Florida, Maryland, Illinois, New Jersey, and Pennsylvania.

THE ALAS MODEL CURVES

One of three ALAS Model calibration curves, using $^{206}Pb/^{207}Pb$ measurements, is shown in Figure 1. Each specific lead isotope ratio is normalized to an NBS standard, then reported relative to an appropriate internal laboratory standard using a "Delta" notation where:

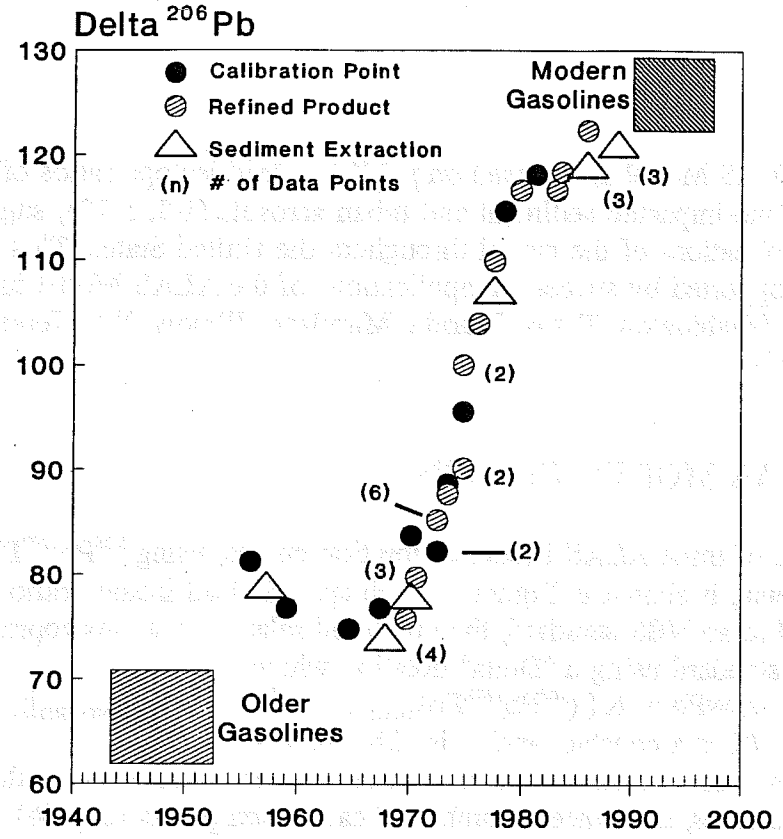
$$\Delta^{206}Pb = K\,[\,(^{206}Pb/^{20X}Pb)_{SAMPLE} - (^{206}Pb/^{20X}Pb)_{STANDARD}];$$

(K is a constant and X is either 4, 7, or 8).

The smooth, well-defined nature of each curve, concordance of results from different matrices, and current number of calibration points (n = 66), indicate model conditions are well-founded. If, for example, significant, long-term variations had occurred in lead isotope ratios of U.S. industrial lead sources, the amount of scatter in the data would increase and systematic variations obscured. Independent checks on ALAS curves are found in published research on time dependent industrial lead isotopic variations (1,3,5,6,9) curves are very similar morphologically, but are not specific to gasoline lead due to their focus on all anthropogenic sources of lead.

AGE RESOLUTION

Uncertainties in the model ages determined by the ALAS curves arise from analytical errors in lead isotope ratio measurements (< 0.1%), errors in the calibration data ages (< 1 year, post-1970; 1-2 years, 1955-1970), slope of the curve, curve fit, and lead exchange reactions (quantifiable via lead isotope - lead concentration mixing models). Typical errors have ranged from 1-2 years for post-1970 events and 3-5 years for events prior to 1970. These errors are a significant improvement over age estimates based on the chronology of gasoline additives or evaluations of hydrocarbon compound aging in soils where degradation kinetics vary as a function of the conditions (e.g. aerobic versus anaerobic; nutrient levels). The summary of gasoline additive chronology (Figure 2) demonstrates that the presence or absence of additives can provide age reolutions no better than 5-10 years.



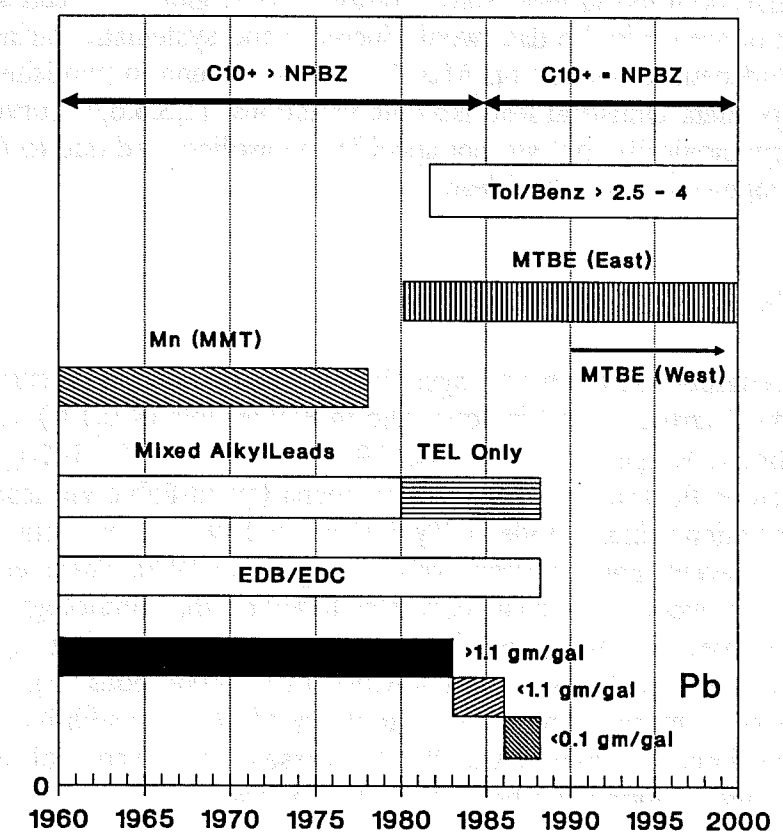


Figure 1. (Upper) Representative ALAS Calibration Curve.
Figure 2. (Lower) Chronology of Gasoline Additives.
Compiled by R.W. Hurst (1)

BACKGROUND/GASOLINE LEAD DISCRIMINATION

The question arises as to how the ALAS Model is applied when lead concentrations are at the "background level". One must differentiate the true, natural background (prior to industrial input) from low levels of lead in soils (typically < 2-20 ppm) which are often misconstrued as "background", when in fact an anthropogenic, i.e. gasoline-derived, component may be present.

Distinctions between natural and anthropogenic lead can only be made using integrated lead isotopic and concentration approaches. Even ppb levels of lead can contain a significant anthropogenic component (9-11). For example, few would argue that lead concentrations exceeding 1000 ppm in soils near a lead smelter were anthropogenic in origin. However, it would be acceptable to determine an average lead concentration on a statistically significant population of soils with "normal" lead concentrations and call this "background" lead for risk analysis purposes. Even "normal" levels of lead in soils may contain an anthropogenic component which can be characterized via sequential extractions and integrated lead isotopic ratio - concentration analyses. The anthropogenic component can then be dated with the ALAS Model.

CASE STUDIES

The case studies discussed below are representative applications of the ALAS Model throughout many portions of the United States.

SOUTHERN CALIFORNIA

Gasoline seepage into an underground parking structure began in the months following an intense period of precipitation. Three local service stations, upgradient of the parking structure, were "identified" as potentially responsible parites or PRPs. Complaints and cross-complaints were filed within weeks of the first incursions. Whose product was it? Despite extensive fingerprinting efforts using gas chromatography, dye analyses, and light stable isotopes, identification of the specific source(s) of gasoline remained equivocal. The presence of lead scavengers, however, suggested it may be an older source.

Samples of the gasoline seeps, free product floating on groundwater, soils in the vicinity of the sites, and dispensed unleaded gasolines from the operating service stations were either collected or provided. Ranges in measured $^{206}Pb/^{207}Pb$ ratios (95% confidence interval about the mean) for the various sample types at the California Test Site are as follows: PRP gasolines,

1.205 - 1.219; free product seeps, 1.177 - 1.182; free product on groundwater, 1.180 - 1.183; soil anthropogenic lead, 1.178 - 1.184; and soil background, 1.190 - 1.192. It is important to note that each of the three PRP unleaded gasolines was isotopically distinct. This is due to the fact that the lead isotopic signature of what we now call unleaded gasolines are derived from those of their crude oil source and refining. Thus, despite the low levels of lead present in unleaded fuels, it is possible to discriminate among different manufacturers products in cases where their crude oil sources differ.

The lead isotope results indicate free product could not have originated from any of the three upgradient service stations (i.e. PRPs) or by lead exchange between PRP gasolines and soil background lead; gasoline - soil lead exchange would result in $^{206}Pb/^{207}Pb$ ratios between 1.219 and 1.190 rather than values ranging from 1.177 to 1.184, i.e those of the free product and soil anthropogenic lead. Free product and soil anthropogenic lead, however, share a common source based on their overlapping lead isotopic ranges.

Resulting ALAS Model ages of free product and soil anthropogenic lead ranged from 1970 to 1975. Title searches and local fire department records indicated a former owner of the site operated a gasoline station from 1969 through 1975, during which time a number of accidental releases of significant volume had occurred. The ALAS Model ages, being consistent with documented gasoline releases at the site, and lead isotopic data, which demonstrated the free product could not originate from any upgradient PRP site, resulted in a dismissal of the charges against the PRP's.

FLORIDA

Hydrocarbon contaminated soils were discovered at a gasoline station that had been operating continuously since the 1940's but had numerous owners over its 50 years of operation. Although available records did not indicate any specific responses by agencies, such as fire departments, to spills at the site, releases may have occurred during pipeline repairs in the 1950's and late 1980's.

Samples of 20 soils were sent for lead isotopic fingerprinting and ALAS Model age determinations. Benzene, toluene, ethylbenzene, and xylene (BTEX) concentration ranges of the soils ranged from non-detectable to thousands of ppm. Each soil underwent three to four sequential extractions using organic solvents followed by dilute acids to remove "young" organic lead (if present) and anthropogenic lead. Residual soil minerals were also analyzed to identify the natural background lead concentrations and associated isotope ratios. Such sequential extractions are invaluable tools in cases where soils may

contain multiple sources of anthropogenic lead; each soil lead source can be characterized via its lead isotopic-concentration signature.

Results of the analyses identified three isotopically distinct sources of lead (endmembers) in the soils: Endmember 1 was characterized by low lead concentrations (2-3 ppm) and high $^{206}Pb/^{207}Pb$ ratios (1.23 - 1.25); Endmember 2 had elevated lead concentrations (> 20 ppm) but low $^{206}Pb/^{207}Pb$ ratios (1.15 - 1.16); Endmember 3 had lead concentrations similar to those of Endmember 1 but lower $^{206}Pb/^{207}Pb$ ratios of 1.21 to 1.22. Endmembers 2 and 3 were restricted to BTEX-impacted soils, and are therefore attributable to gasoline releases. Endmember 1, associated with soil mineral residues and unimpacted soils, is the natural background lead.

Ages derived from the ALAS Model indicated lead in Endmember 2 dated back to the mid-1950's. The lead isotopic characteristics of Endmember 3 are consistent with those of modern, unleaded gasolines (post-1988), a suspected contaminant at the site. The results corroborated the suspected gasoline release site history and demonstrated the applicability of the ALAS Model to soils with multiple anthropogenic, mixed lead isotopic signatures.

VERIFICATION OF BIOREMEDIATION

Lead isotope ratios and the ALAS Model are now being integrated with biogeochemical data from sites undergoing bioremediation. Specifically, we have been investigating relationships between lead and carbon isotopes (e.g. $\delta^{13}C$) in order to evaluate time frames of bioremediation.

One investigation in progress involves the monitoring of soil vapor carbon isotopic signatures and lead isotopic/concentration characteristics of a ten to fifteen year old gasoline plume. Relative to archived samples of the original gasoline product, $\delta^{13}C$ values of soil vapor emanating from the plume have become heavier by 3 to 4 per mille (-28.8 to -25) while lead isotope ratios of the free product in the plume have varied by less than 0.2% despite significant drops in lead concentrations. The carbon isotopic shift is of similar magnitude to those reported in the literature (7) for aerobic biodegradation of petroleum hydrocarbon products.

These are initial results from a pilot study. However, our long-term objective is to model time frames of intrinsic bioremediation using covariations among isotope ratios, organic compounds, and trace elements analyzed in biogeochemical samples.

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FIELD INVESTIGATIONS UTILIZING A SITE CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM (SCAPS) COMBINED WITH GAS CHROMATOGRAPHY

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In order to expedite environmental soil and groundwater investigations, the US Army Corps of Engineers, in conjunction with the Air Force and Navy, has recently developed SCAPS (Site Characterization and Analysis Penetrometer System). This system incorporates two isolated compartments mounted to a Kenworth truck chassis. One compartment houses a penetrometer system while the other serves as a control center, housing computer and analytical equipment. The system has two cone penetrometers to make in situ measurements; one measures laser induced fluorescence (LIF) along with soil strength/classification, while the other measures soil electrical resistivity in addition to soil strength/classification. The penetrometer system allows for the collection of subsurface soil samples as well as the rapid installation of temporary groundwater monitoring wells with minimal waste generation. The US Army Corps of Engineers has combined SCAPS technology with a portable gas chromatograph (GC) to allow on-site characterization and delineation of contaminants such as volatile organics and petroleum products. The features associated with the SCAPS/GC system provide for a faster and more effective characterization of environmental sites when compared to traditional field investigations.

INTRODUCTION

Traditional environmental site characterization represents a significant portion of remediation efforts, employing such methods as drilling, sampling and laboratory analysis. Delineation of subsurface contamination requires substantial effort and expense, involving soil gas and topographical surveys, soil borings, the installation of ground water monitoring wells and extensive sample collection. In order to provide a rapid and cost effective means of characterizing Department of Defense (DoD) sites currently undergoing restoration (cleanup) the U.S. Army Corps of Engineers Waterways Experiment Station (WES) under the sponsorship of the U.S. Army Environmental Center (AEC) initiated the development of the Site Characterization and Analysis Penetrometer System (SCAPS). Under the Strategic Environmental Research and Development Program (SERDP), WES partnered with the U.S. Naval Command, Control and Ocean Surveillance Center and the U.S. Air Force Armstrong Laboratory to accelerate the research and development of SCAPS (1-4).

Currently seven SCAPS units have been produced and are undergoing field trials. The Tulsa District of the U.S. Army Corps of Engineers has been utilizing one such unit in conjunction with field gas chromatography (GC) to provide rapid on-site delineation of volatile organic contamination (VOC) plumes. This combination was utilized to further delineate the extent of trichloroethene (TCE), tetrachloroethene (PCE), 1,2-dichloroethane (1,2-DCA), cis and trans 1,2-dichloroethene (c &t DCE) as well as various other volatile organic contaminants in the shallow groundwater at Longhorn Army Ammunition Plant (LHAAP) after a traditional investigation identified the presence of these contaminants. Thus a unique opportunity exists to compare the traditional method of investigation with the advantages of the SCAPS program. This presentation will discuss the results of such a comparison.

EXPERIMENTAL

The SCAPS unit consists of two stainless steel compartments mounted on a Kenworth chasis. The penetrometer push system is housed in the forward compartment and consists of a Hogentogler, Inc. penetrometer system. The instrumentation compartment houses the computer system, communications equipment and soil fluorometer instrumentation (3). Currently the system is equipped with two cone penetrometers (sensors); one measures laser induced fluorescence (LIF) (5) along with soil strength/classification, the other measures soil electrical resistivity as well as soil strength/classification. The LIF system utilizes the 337.1 nm line of a Photon Technology International PL2300 nitrogen laser to excite polynuclear aromatic hydrocarbons with the resulting fluorescence being analyzed by an EG&G Optical Multichannel Analyzer III™. SCAPS has the capability of collecting soil

samples with a Mostap or Hogentogler™ sampler and water samples via utilization of HydroPunch II™ or Power Punch devices. The Power Punch is capable of setting small diameter monitoring wells. Samples are collected from these wells through the use of a Teflon or stainless steel bailer.

The gas chromatograph (GC) is a Scentograph "Plus II" portable field unit. The unit is equipped with a Micro Argon Ionization Detector (MAID), Electron Capture Detector (ECD) as well as an Argon Ionization Detector (AID). For the field investigations, a MAID detector was set to allow for sub parts per billion (ppb) range of volatile hydrocarbons such as TCE and PCE. The GC is equipped with a 30 meter Restek MXT-Volatiles column with Argon being used as the carrier gas. An IBM PS2 laptop computer controls the system. The GC system is equipped with a purge and trap apparatus to expedite the analysis of samples. The compactness of the system allows for it to be set-up in a limited amount of space.

RESULTS AND DISCUSSION

A multi-phase investigation of 125 in-ground concrete storage tanks (sumps) and 20 waste rack sumps located throughout the Longhorn Army Ammunition Plant (LHAAP) production area was conducted by the U.S. Army Corps of Engineers (USACE), Tulsa District. Phase I of this investigation consisted of drilling subsurface borings to investigate potential soil contaminants adjacent to all 145 sumps. Analytical results from the first phase of the investigation confirmed the presence of several organic contaminants in the subsurface soil (6). Based on these findings, a second phase of remedial investigations was recommended to determine if groundwater had been impacted.

Phase II of the project required the installation of seventy-one traditional groundwater monitoring wells (7). These wells were installed to determine the extent, if any, of the groundwater contamination. As Table I shows, the installation of these seventy-one traditional wells required two drill rigs, between 6 and 15 people, working 10 hour days approximately two months to complete the project. Likewise, this method generated approximately four hundred drums of investigation derived waste (IDW). A total of seventy-one groundwater and 280 soil samples were collected and sent off for analysis. These samples were analyzed for the presence of volatile and semi-volatile organic compounds, metals, explosives, total petroleum hydrocarbon and cyanide. Based on the findings of this investigation (see Figure 1) it was determined that the number of monitoring wells installed was not sufficient to fully delineate the areas of contamination in the groundwater. Figure 1 displays the contamination plume map based on the findings of the phase II investigation.

As pointed out earlier, installation of traditional groundwater monitoring wells is time consuming, expensive and inexact. In order to ensure correct placement of

new monitoring wells to be installed in a subsequent investigation, Phase III, it was decided to utilize SCAPS technology to fully delineate the lateral extent of the groundwater contamination, thus a Pre-Phase III project was initiated. The Pre-Phase III project resulted in the installation of one hundred twelve temporary groundwater monitoring wells (8). Total project time using a SCAPS field crew of 4 to 8 people was 15 days. The only IDW generated during this project was due to decontamination of equipment, GC standards and sample collection, which amounted to approximately three 55 gallon drums of waste.

Table I provides a comparison between the Phase II and Pre-Phase III projects. As Figure 2 shows, the Pre-Phase III SCAPS push points (temporary well locations) provide a greater resolution of the contamination plume(s). In fact the SCAPS work seems to indicate that most sumps were responsible for small individual plumes which combined with each other to form the large plumes shown in Figure 2. These results will be used in situating the permanent ground water monitoring wells at the sites indicated in Figure 2.

It would be beneficial to discuss the costs listed in Table I. In particular, the types of samples and their analysis should be addressed. For instance, in the analysis of groundwater a more representative cost comparison would be based solely on the volatile organic analysis. Based on costs for EPA method 8260 (9), as provided by the U.S. Army Corps of Engineers South Western Division Laboratory, the Phase II volatile organic analysis would have cost $12,070.00 compared to $2,040.00 for the analysis of quality assurance samples taken in Pre-Phase III work. The cost savings between SCAPS and traditional methods is difficult to discern in the area of geotechnical samples and analysis. The SCAPS system provides soil classification based on resistivity probe pushes, thus no soil samples were collected in the Pre-Phase III work. However approximately 5 CPT (cone penetrometer resistivity sensor) pushes were made to characterize the soil at LHAAP. The Phase II work analyzed 460 Geotechnical samples (7). SCAPS greatest cost savings is associated with IDW generated during an investigation. As Table I reveals, the approximately 400 IDW soil and water drums of Phase II cost an estimated $500,000.00 to dispose of, compared with $1500.00 for the 3 drums of waste water associated with decontamination of equipment and GC standards for the Pre-Phase III project.

Table II lists the results of the quality assurance samples in comparison with the GC field results. Due to the need for rapid analysis in the field, the samples were run using a two point calibration curve, per Syntex Inc. recommendations. The computer program sets zero as one point in the calibration curve, with the upper limit (point) being selected by the field analyst. In all instances the maximum limit was set at 50 ppb using a standard solution made in the field. Although it is extremely difficult to accurately measure widely varying concentrations (e.g. ppb versus ppm range) Syntex states this technique provides results which are within 10 to 20% of

the true value, depending upon how close the concentration of the sample is to that of the standard (10). As the results in Table II demonstrate, most of the field data are in good agreement with the quality assurance results. Significant differences do occur in a few samples (i.e. S-3-04 and S-S-05). However, it is important to remember that this is a field screening method and the data generated are used primarily to identify the presence and magnitude of contamination. In this respect the field screening provided by the GC was an unqualified success, with only two samples exhibiting false negative results (S-3-01 and S-3-08), both of which had contaminates in the low parts per billion range. Finally, it should be noted that some of the differences between the field GC and quality assurance laboratory results can be attributed to the limitations of the GC technique. In several instances unknown compounds (those for which the GC was not calibrated) co-eluted with the "known" contaminates. In such instances the GC is incapable of separating the contributions from each contaminant.

Soil classification is accomplished using the soil strength measurements (cone tip and sleeve friction) obtained when performing a static push with either standard SCAPS probe. A computer alogrithm is used to map the corrected cone tip and sleeve friction parameters onto the soil classification chart with the resulting output being a Soil Classification Number (SCN) which correlates to the soil types. For instance, a SCN of 0.5 is a typical clay, the range of SCN's of 1 to 2 represents silt mixtures, SCN's for sands range from 2 to 4, and a fine sand has a SCN between 2.5 and 3.5. The SCN chart is automatically displayed during the penetrometer push and is output in the data set after each penetrometer push.

CONCLUSIONS

Complete delineation of subsurface contaminants usually requires trial-and-error placement of a significant number of monitoring wells. SCAPS in conjunction with GC technology can provide a rapid and cost effective alternative to this current methodology by providing lateral delineation of contaminants for accurate groundwater monitoring well placement. As shown here, use of SCAPS as a field screening technology expedited the determination of the lateral extent and possible source areas of groundwater VOC contamination, and provided a process by which minimal analytical costs were incurred (8). In addition to soil classification and LIF (petroleum, oils and lubricants sensor) capabilities, current efforts are underway to develop in situ sensors capable of detecting explosives, volatile organic hydrocarbons and metals (using Laser-induced breakdown spectroscopy). Similarly sampling efforts are being advanced through the development of a multiport sampler. This device will allow for multiple samples to be collected from a single penetrometer push. As one can see indirect push technology, as evidenced by SCAPS, is still in its infancy but it promises to revolutionize environmental site characterization.

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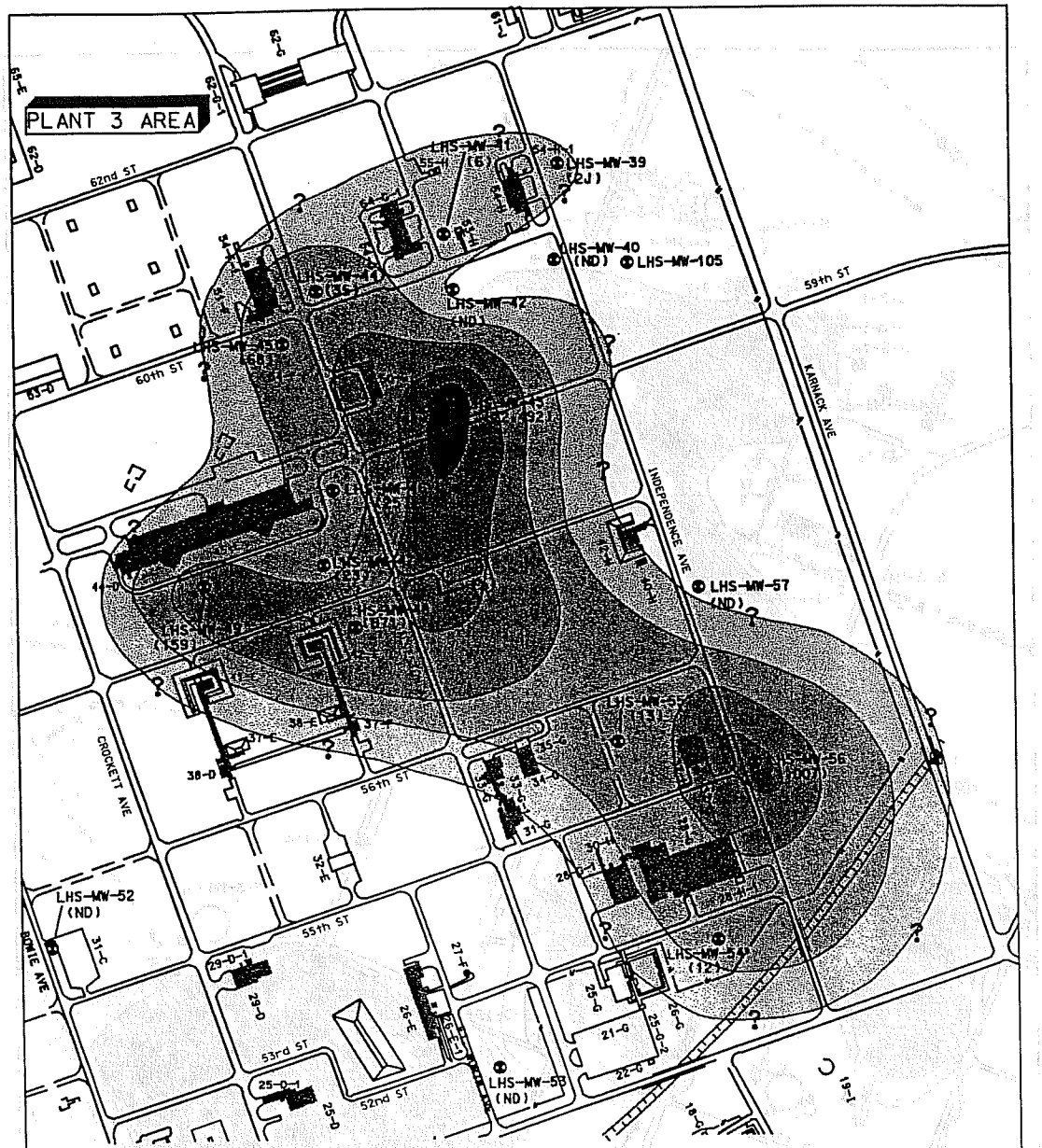

LEGEND

TOTAL CHLORINATED ALIPHATIC HYDROCARBONS CONCENTRATION VALUES IN ug/L (BASED ON 1995 SAMPLE RESULTS)

- 1-10
- 10-100
- 100-1,000
- 1,000-10,000
- 10,000-

- GOOSE PRAIRIE CREEK SAMPLING POINT
- MONITORING WELL LOCATION
- (ND) GROUNDWATER SAMPLE RESULTS - ug/L

Figure 1. Phase II Traditional Monitoring Wells

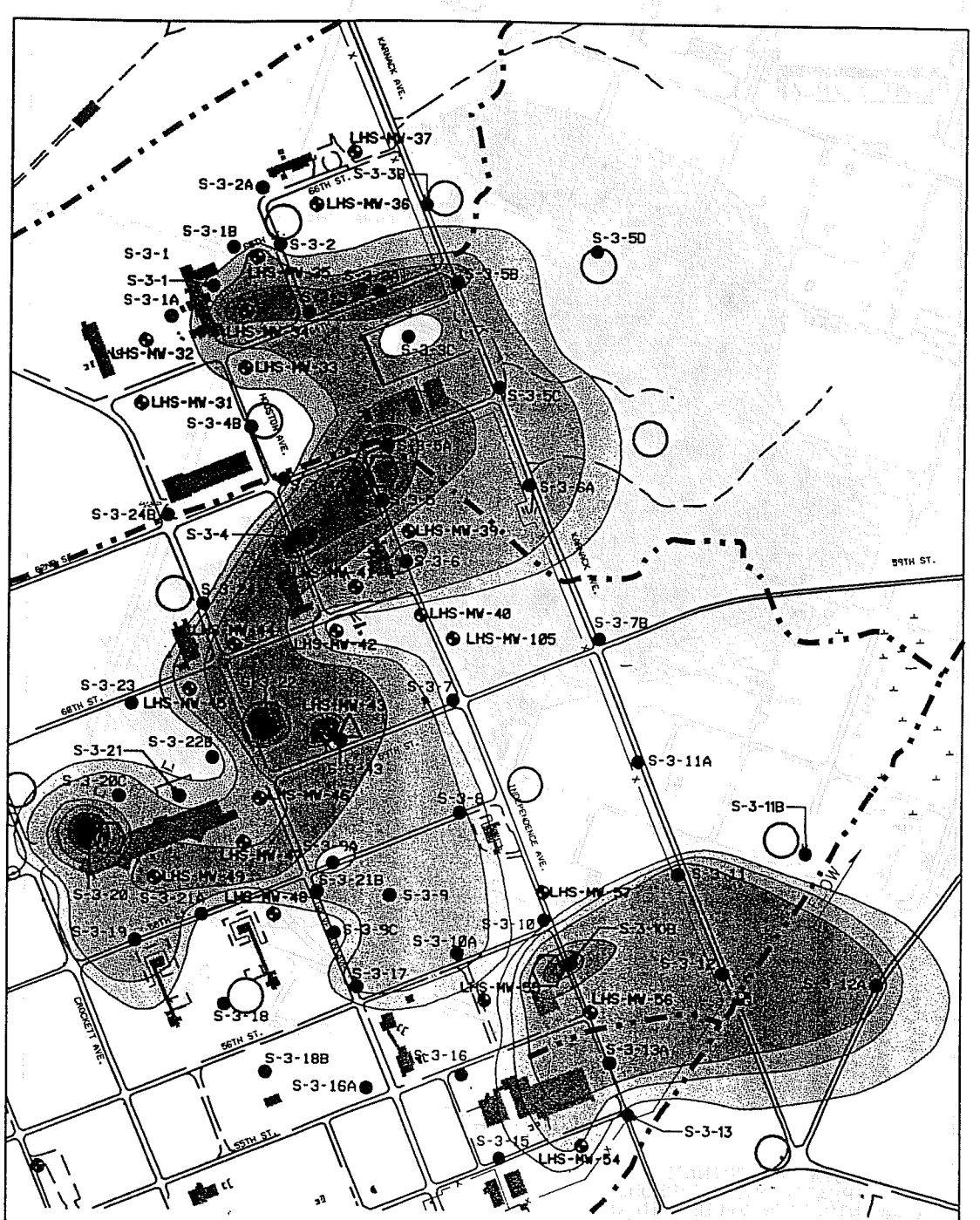

Figure 2. Pre-Phase III SCAPS Monitoring Wells

Table 1

Comparison of Traditional Investigation versus SCAPS

Project	Phase II (7)	Pre-Phase III (8)
Intent of Work:	Determine if groundwater had been contaminated.	Delineate lateral extent of groundwater contamination.
Approach	Traditional monitoring wells	SCAPS technology
Number of Wells	71	112 (Temporary)
Number of groundwater samples	71	112
Number of Geotechnical Samples	460	4 to 5 CPT pushes with SCAPS
Analytical Methods	VOCs, SVOCs, Metals, Explosives, TPH, Cyanide	VOCs (GC Scan)
Geotechnical Tests	Soil classification, moisture, atterberg limits, sieve analysis	Resistivity (SCAPS)
Supplies (Drilling and Sampling)	~$60,000	~$10,000
Drill Rigs and Crews	~$231,000 (2 Crews)	~$45,000 (1 SCAPS)
Employees on site	6 to 15	4 to 8
Duration (Days)	~60	15
Analytical Costs for Water	$12,070 ($70,000 all parameters)	$2,040
Validation Costs	$97,000 (includes all samples)	$1,000
Number of IDW Drums Generated	~400	3
Other Field Labor	~$90,000	~$30,000
Cost for Waste Management	~$500,000	~$1,500
End Result	Contamination found in groundwater	Lateral extent of contamination delineated
Field Work Costs	$990,070 VOCs only ($1,048,000 total cost)	$89,540

Table 2

Comparison of Field and Laboratory Quality Assurance Results (8).

Sample ID	Site	Analyte Concentrations (ppb)					
		t DCE	c DCE	1,2 DCA	TCE	PCE	Tentatively Identified Compounds (TICs) (ppb)
S-2-07	Field	56	1900	400	>3200	21	1 Hit
	Lab	77	725	ND	3325	54	chloroform @ 8.1, 1,1-dichloroethene @ 58; 1,1,2-trichloroethane @1.4; Vinyl chloride @ 190
S-3-01	Field	ND	ND	ND	ND	ND	
	Lab	ND	ND	ND	10.4	ND	TIC 3 @ 554; TIC 1 @ 336; TIC 2 @ 1892
S-3-03	Field	17	59	ND	16	1	Broad Peak
	Lab	ND	54	ND	40	8.5	Dichlorodifluoromethane @ 577; 1,1-dichloroethene @18.9; TIC 3 @ 24.8; TIC 1 @ 167 ; TIC 2 @ 2195
S-3-04	Field	ND	ND	ND	>60,000	ND	
	Lab	1.5	81	ND	15015	ND	chloroform @ 3.0; 1,1-dichloroethene @ 24.8; 1,12-trichloroethane @ 2.5; Vinyl chloride @ 2.1; TIC 2 @ 127
S-3-08	Field	ND	ND	ND	ND	ND	
	Lab	ND	ND	ND	29.5	ND	TIC 2 @ 104
S-3-12	Field	ND	24	ND	480	ND	
	Lab	ND	37.4	ND	521	ND	1,1-dichloroethene@3.7; vinyl chloride @ 4.9; TIC 2 @ 602
S-3-19	Field	ND	1	28	8	ND	
	Lab	ND	2.7	1.7	38.3	ND	1,1-dichloroethene @ 1.7; TIC 2 @ 192
S-3-20	Field	66	250	ND	>30,000	ND	
	Lab	61	932	ND	55200	ND	chloroform @ 21.2; dichlordifluoromethane @ 13.1; 1,1-dichloroethene @ 47.9; methylene dichloride @ 25; vinyl chloride @ 30.5; TIC 2 @ 94
S-S-05	Field	ND	ND	342	3	ND	1 Hit
	Lab	ND	1.7	7.4	12.7	ND	1,1,-dichloroethane @ 29.6; 1,1-dicholoroehtene @ 298; 1,1,2-trichloroethane @ 1.5; vinyl chloride @ 2.1

ND-analyte not detected, TIC 1 -1,1,2-trichloro-trifluoroethane or CFC-113, TIC 2 - acetone, TIC 3 - 1,2-dichloro-1,1,2-trifluoroethane.

Bioreactor for Treatment of BTEX-Contaminated Groundwater: A Case History

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A packed-bed bioreactor is being used to remediate BTEX- (i.e., benzene, toluene, ethylbenzene, and xylene) contaminated groundwater at a gasoline station site in North Carolina. The bioreactor utilizes a proprietary adsorbent biocatalyst support developed by E. I. du Pont de Nemours and Company. The biocatalyst support contains internal macropores which are used to immobilize BTEX oxidizing microbes by physical entrapment. The overall system design and operations history, including data from the North Carolina site, is discussed in this paper. The economics of the bioreactor are compared to air stripping and activated carbon adsorption.

INTRODUCTION

EPA has estimated that over 300,000 sites exist where hydrocarbon spills have contaminated soil and groundwater. It is likely that natural, as opposed to active remediation (i.e., an engineered system), will be the best cleanup strategy at many sites; for example, sites with low health risks, and where time is available for natural attenuation processes to occur. However, sites with higher risk factors will require active remediation and the potential liability associated with ownership of a contaminated site will motivate many active cleanup projects. Therefore, the cost-effective remediation of hydrocarbon spills from leaking underground storage tanks and pipelines continues to be a major engineering challenge.

Towards developing a more cost-effective means of cleaning up contaminated sites, the DuPont Company has developed an advanced bioreactor technology known as the Bio-Sep™ bioreactor. The bioreactor is a cost-effective alternative to the more conventional methods of treatment, e.g., air stripping and/or granular-activated carbon (GAC). The Bio-Sep™ bioreactor provides on-site destruction of potentially hazardous organics, and virtually eliminates air emissions and solids waste (e.g., GAC).

This paper discusses the application of a Bio-Sep™ bioreactor at a retail gasoline station and convenience store in North Carolina. The station is located in a heavily developed area that is bounded on all sides by a mix of residential and business properties.

THE BIO-SEP™ BIOREACTOR

The Bio-Sep™ bioreactor for groundwater remediation has been implemented primarily in a packed-bed to an expanded-bed operating mode. The Bio-Sep™ bioreactor incorporates spherical 2- to 3-mm-diameter pellets (i.e., Bio-Sep™ beads) that are engineered from a composite of 25% aramid polymer and 75% powdered activated carbon. Bio-Sep™ beads uniquely combine three physical characteristics in a single biocatalyst support: (1) high internal macroporosity which is enveloped by a membrane structure, (2) high adsorption capacity from the integral activated carbon, and (3) durability and strength from the polymer binder.

Figure 1 shows a cross-section of a Bio-Sep™ bead. The dark regions are 0.2- to 0.5-mm-diameter macropores. The surface of the bead consists of a membrane structure, approximately 0.1 mm in depth, which contains 2- to 10-micron pores which penetrate the surface (similar to an ultrafiltration membrane). The surface pores allow individual

bacteria to enter the internal macropores where they can grow into densely packed colonies. The following details other physical characteristics of Bio-Sep™ beads:

Porosity	75-80%
Intrusion Volume	1.8 - 2.5 cc/g
Adsorption Capacity	>600 sq.m./g
Dry Bulk Density	0.16 g/cc
Compression Strength	10% bed compression at 80 psi

The high degree of internal macroporosity, enveloped by a membrane structure, allows microorganisms to become immobilized by entrapment. Bio-Sep™ technology does not rely on developing a biofilm on the surface of a material. Nonfloc-forming bacterial cultures can be immobilized within the internal macropores where they are protected from hydrodynamic shear forces and potential predators (e.g., protozoans) which cannot penetrate the relatively small surface pores.

The physical characteristics of Bio-Sep™ beads make them uniquely suitable for managing variations in hydraulic and organic loading rates that are typical of groundwater P&T operation. Due to the membrane structure surrounding the macropores, Bio-Sep™ beads resist dehydration. This allows active microorganisms to be stored in a bed free of external water for long periods of time. Therefore, periodic shutdowns of water flow do not cause a disruption in system performance. Since the bacteria are immobilized by entrapment, washout of bacteria is not a concern. The high concentration of activated carbon helps to buffer the variations in organic loading.

NORTH CAROLINA SITE PROJECT HISTORY

In 1989, a leak was discovered in a product line supplying unleaded gasoline to the dispenser pumps. A site investigation discovered that gasoline had impacted groundwater beneath the site at contaminant concentrations requiring corrective action. The detected concentrations of benzene dissolved in groundwater ranged as high as 13,000 µg/L with total BTEX ranging to 53,000 µg/L.

The plan for corrective action included air sparging and soil vapor extraction for *in situ* remediation. In addition, the presence of nearby, off-site water supply wells necessitated implementation of pump-and-treat (P&T) technology to contain the contaminant plume. Difficulties in obtaining a sewer discharge permit steered the project towards obtaining an NPDES permit allowing discharge of treated recovered groundwater to a local surface drainage. The NPDES permit required a treatment system consisting of an oil/water separator, an air stripper, and activated-carbon adsorption. A P&T system was designed on this basis to treat an anticipated flow rate of 5 GPM.

Brown & Root Environmental assumed management of the project after the Corrective Action Plan (CAP) had already been approved. The state regulators expressed reservations about the efficacy of bioreactors for P&T applications based on their experience with bioreactors supplied by other vendors. Also, this was the first project which had proposed to use the Bio-Sep™ bioreactor in North Carolina. Therefore, the state required that all components of the initial CAP be implemented: (1) air sparging, (2) soil vapor extraction, and (3) P&T for plume containment using air stripping and carbon adsorption for treatment of recovered groundwater. The state allowed the use of Bio-Sep™ in addition to the approved treatment system for demonstration purposes. Therefore, the main objective of this project was to prove the efficacy of the Bio-Sep™ bioreactor so that it could be more readily accepted for approval in future CAP's.

Figure 2 shows the configuration of the P&T system. The bioreactor was placed between the oil/water separator and the air stripper. Bag filters are used to remove solids before and after the bioreactor, and a cartridge type filter is used to remove solids prior to the activated-carbon drums. Compressed air is fed to the bottom of the bioreactor through a porous metal tube sparger to supply oxygen.

The system began operation in late October, 1995. At that time, the bioreactor was inoculated with about 6 L of activated sludge from a refinery wastewater treatment plant.

RESULTS

Although the system was designed to treat a flow rate of up to 5 GPM, the aquifer never yielded this flow rate. The flow rate has averaged about 1.1 GPM since the beginning of the project. Instantaneous flow rates of 2 to 3 GPM have been maintained for periods of a few days. To date, a total volume of over 400,000 gallons of water have been treated at the site.

The influent concentration of benzene to the bioreactor has generally been in the range of 1 to 2 mg/L, and the total BTEX in the range of 5 to 6 mg/L. The bioreactor has maintained a high removal efficiency of all BTEX compounds since the beginning of operations. An initial removal efficiency of greater than 99.5% could have been partially due to the adsorptive capacity of fresh Bio-Sep™ beads. Removal efficiencies have remained mostly in the 90% to 95% range with few exceptions. The monthly performance data for the bioreactor is presented in Figure 3.

DISCUSSION

The bioreactor receives its oxygen supply from the air compressor that is used for the *in situ* sparging operation. Reductions in removal efficiency have been attributed to air compressor mechanical problems and frequent power failures. It is believed that, during these periods, the bioreactor was subjected to anaerobic conditions for periods of up to two weeks.

Although the P&T system is generally low maintenance, solids fouling problems have required frequent change out of filter elements. The bag filter prior to the bioreactor (the primary filter) has been clogged repeatedly by solids originating in the recovery wells and in the oil/water separator. Microscopic and elemental examination of the solids from the primary bag filter indicate that they are primarily slime-forming bacteria. A biofilm has periodically developed on the corrugated surfaces of the oil/water separator, which eventually causes pluggage of the primary bag filter. It is believed that the biofouling problems observed in the oil/water separator and the primary bag filter can be attributed to the *in situ* sparging operations, which are generating biomass within the aquifer. Chemical treatments to combat the fouling problems, such as chlorination of the recovery wells, were not performed because of concerns that an overdosage would be detrimental to the viability of the organisms in the bioreactor.

Other fouling problems have occurred at the filter following the bioreactor, and at the filter following the air stripper. Elemental analysis of these solids indicates that they contain a high percentage of metals (e.g., Fe, Ca, Si) indicating that inorganic precipitates, in addition to biofouling, is a concern at these points in the process. Handling of inorganic precipitates is a common problem with air stripper technology. Filtration of the water is necessary to prevent premature fouling of the carbon canisters - the last treatment unit prior to discharge as required by the NPDES permit.

CONCLUSIONS AND RECOMMENDATIONS

The Bio-Sep™ bioreactor has demonstrated good removal efficiency for BTEX contamination despite the difficulties associated with failure of the oxygen supply and solids fouling problems. An automatic backup system (e.g., compressed air) could keep the reactor aerobic during periods of mechanical or power failure. The high maintenance associated with solids fouling of equipment may be reduced by improving the filtration equipment capacity. However, a better solution may be to reconfigure the treatment process to allow the treated-recovered-water to be recycled into the contaminated zone so that microbes in the water could provide further benefit to the *in situ*

remediation process, and so that the water would not need extensive filtration/GAC polishing in order to meet stringent NPDES permit requirements.

In some states it is possible to return treated-recovered-water to the subsurface with a proper discharge permit. The discharge permits, in some instances, allow the return of water containing hydrocarbons as long as the treatment process meets a specified removal efficiency. For example, in North Carolina it is possible to obtain what is called a "Non-Discharge Permit" for subsurface reinjection of remedial system effluent. Non-Discharge Permits have been granted for removal efficiencies of 90%. The removal efficiency demonstrated by the Bio-Sep™ bioreactor are in the proper range to meet the requirements of the Non-Discharge Permit of North Carolina.

Figure 4 shows a conceptual diagram of the suggested system configuration. Groundwater is pumped from recovery wells placed near the perimeter of the hydrocarbon plume. The recovered water is passed through the Bio-Sep™ reactor and then returned to the subsurface through an infiltration gallery, which resembles the leach field of a septic system. A key to the strategy is to place the infiltration gallery in the heart of the contaminated zone, the so-called "Hot-Spot," so that the population of hydrocarbon-degrading bacteria is boosted in the zone where it is needed most. Continuous recirculation of groundwater through the system would promote microbial contact with hydrocarbons both within the controlled environment of the Bio-Sep™ bioreactor and within the subsurface. With time and with proper design, the infiltration gallery would become an extended bioreactor serving as a subsurface incubation cell to more fully populate the entire hydrocarbon-impacted zone. Addition of nutrients and electron acceptors could be easily implemented with this design.

An advantage of the proposed system configuration, compared to other bioremediation strategies, is that a microbial population acclimated to the site groundwater conditions is produced in the controlled environment of an aboveground bioreactor. By returning the biomass to the subsurface, the strategy provides a means to accelerate the start-up of the *in situ* process. The technology may prove to be especially beneficial when dealing with relatively recalcitrant compounds such as chlorinated organics. The buildup of the *in situ* microbial population due to the *ex situ* bioreactor could continue to enhance the *in situ* remediation process for periods of time even after the external recirculation flow ceases. Applying the Bio-Sep™ bioreactor to quickly build the *in situ* microbial populations may help ensure a faster start to the natural attenuation processes and shorten the time requirement to meet cleanup goals.

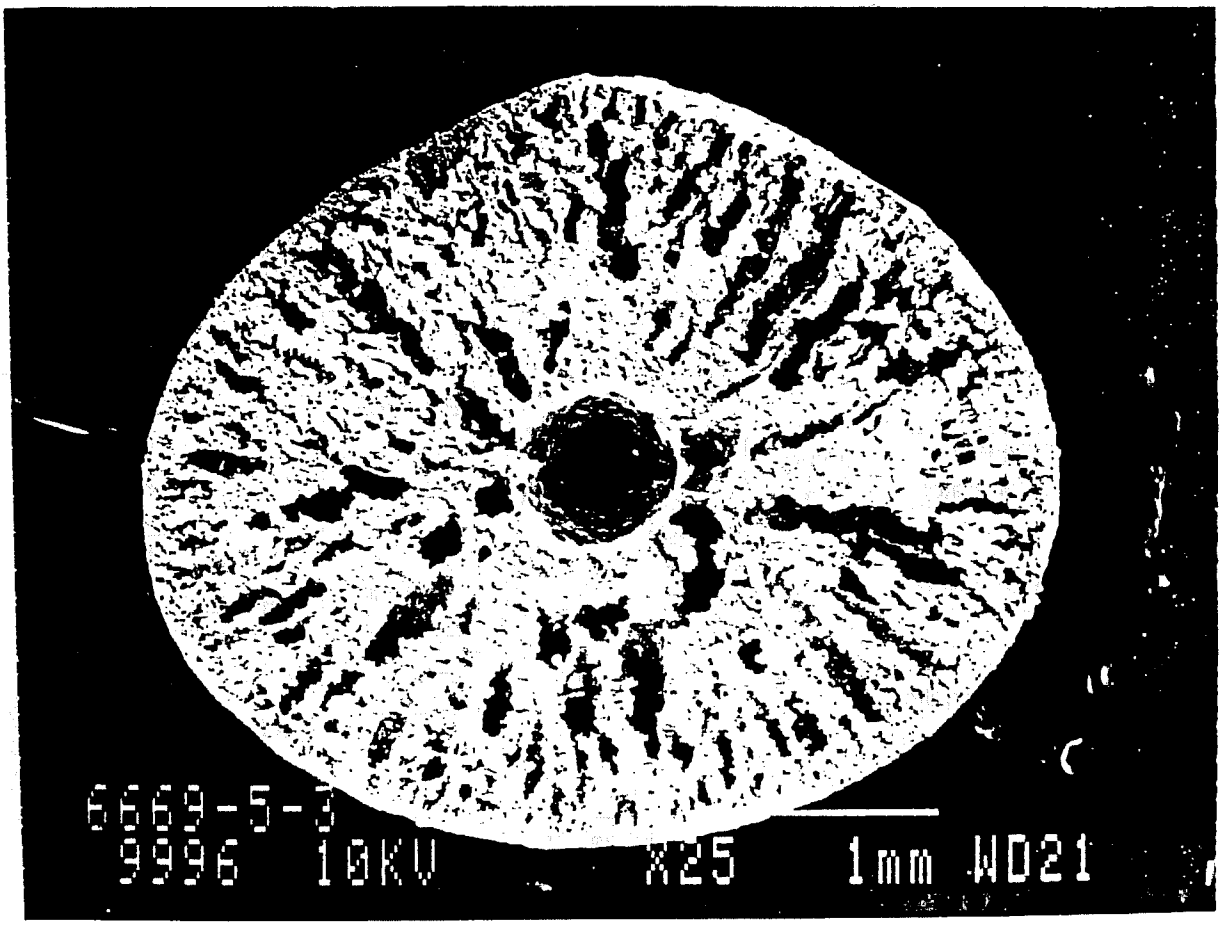

Figure 1: Cross-section of Bio-Sep™ Bead

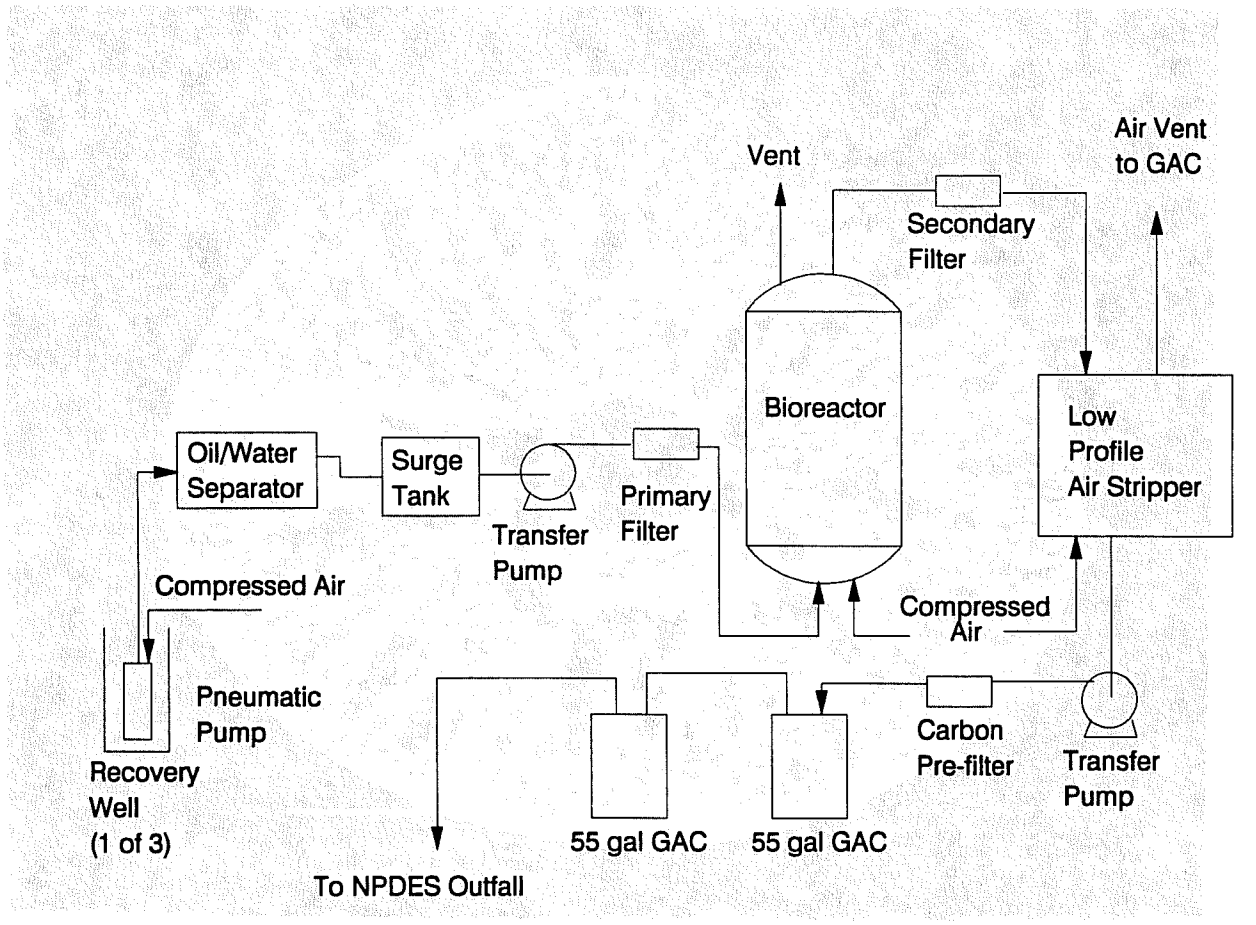

Figure 2: Flow Diagram of Pump-and-Treat System

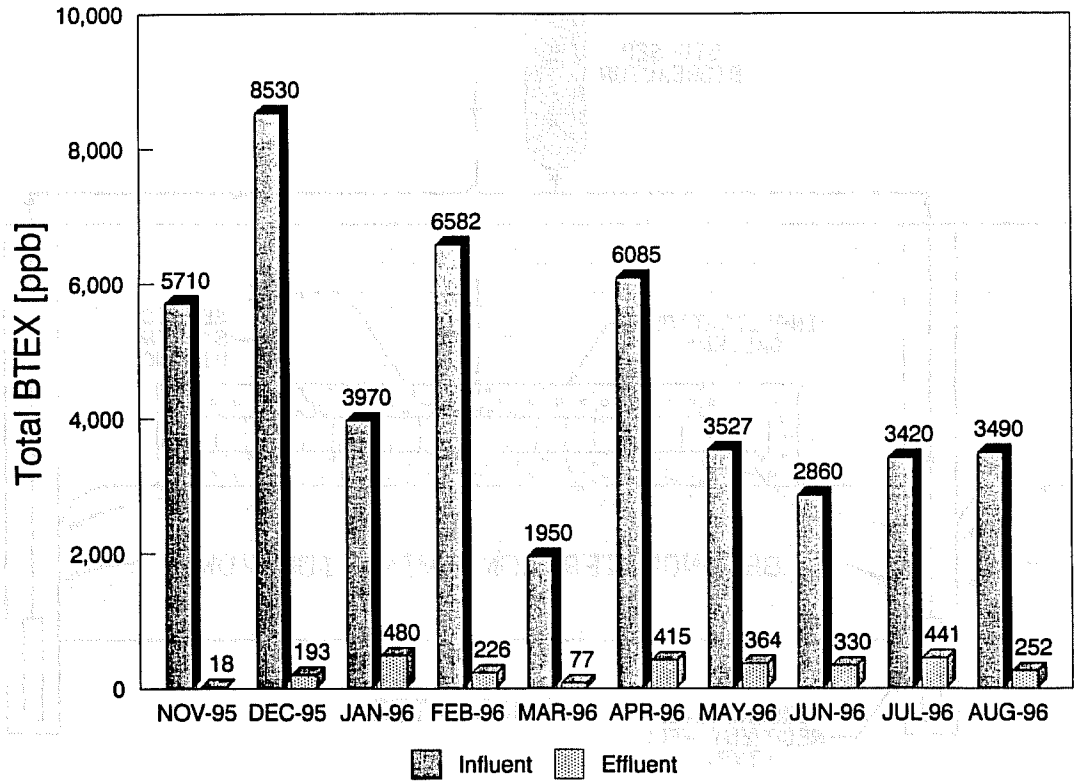

Figure 3: Bio-Sep™ Performance

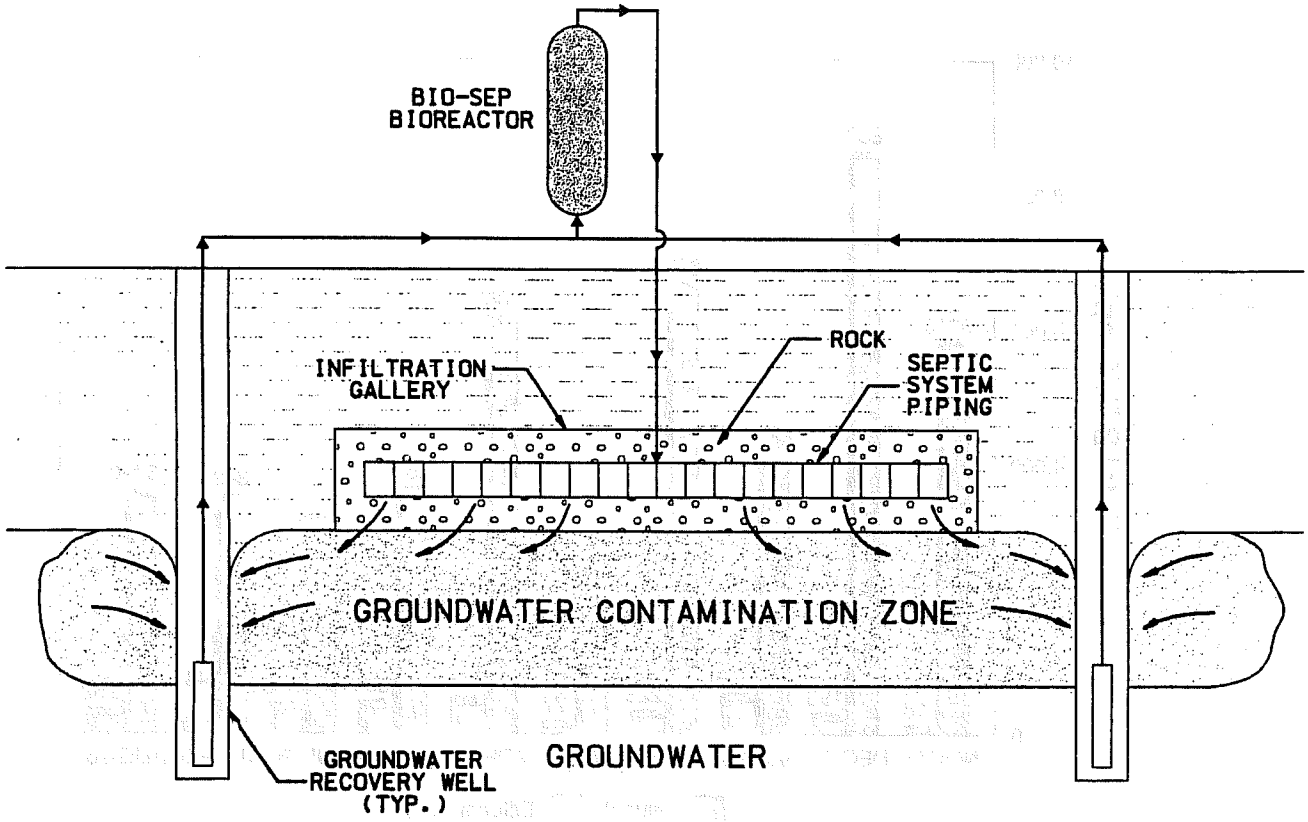

Figure 4: Schematic of Bio-Sep™ System Reconfiguration

Use of Air Sparging and Soil Vapor Extraction to Remediate Dissolved, Adsorbed, and Separate Phase Heptane

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An existing manufacturing facility formerly stored heptane in five USTs. Following a release in September 1989, 12 monitoring wells and seven recovery wells were installed as part of a groundwater pump and treat remediation system. The primary concern is separate phase heptane, although dissolved concentrations of BTEX have also been reported in groundwater. Tenneco Business Services (TBS) and *SECOR* became involved with this project in 1994. The efficiency of the groundwater recovery system had decreased with time, resulting in limited recovery of separate phase heptane. TBS and *SECOR* recommended that an AS/SVE system be installed to more expeditiously and cost effectively remediate the area. The system consists of 26 sparge and vertical vapor extraction points plus one 135 feet long horizontal SVE recovery line, and covers an area of approximately 4.5 acres. The SVE system was put into operation in December 1995, while the AS component was brought on-line in June 1996. After almost nine months of operation, approximately 62,000 pounds of non-methane hydrocarbons (approximately 10,930 gallons) have been removed from the subsurface. The results of this study demonstrate the need to periodically review the efficiency and cost effectiveness of operating remedial systems, especially in light of the changing nature of technology, regulatory requirements, and the environment.

INTRODUCTION

An existing manufacturing facility uses heptane as a solvent to remove lubrication oil from aluminum during its re-milling processes. The heptane was formerly stored in five underground storage tanks (USTs) with a total capacity of 34,000 gallons. In September 1989, it was discovered that a release of heptane had occurred from an underground product line. The five USTs were subsequently removed from service and replaced with above ground storage tanks. As a result of this release, a groundwater recovery and treatment system was installed, and a National Pollutant Discharge Elimination System - Discharge to Groundwater (NPDES-DGW) permit was issued. The groundwater recovery and treatment system, which had been in operation since 1990, consisted of seven recovery wells, an oil/water separator, and a low profile air stripper. The treated groundwater was re-injected through an infiltration gallery.

In addition to the seven recovery wells (RW-1 through RW-7), a total of 12 monitoring wells (MW-1 through MW-12) were installed along the east side of the facility (Figure 1). The primary compound of concern is separate phase heptane which has commonly been detected in six of the monitoring wells (MW-4, MW-5, MW-6, MW-8, MW-9, and MW-12) and three of the recovery wells (RW-1, RW-4, and RW-5). Detectable concentrations of benzene, toluene, ethylbenzene, and/or xylenes (BTEX) have also been found in the monitoring wells that do not contain non-aqueous phase liquids (NAPLs). Only low concentrations of dissolved phase heptane have been found in the monitoring wells at the site, which is consistent with the low solubility of heptane in water.

Tenneco Business Services (TBS) and SECOR International Inc. (*SECOR*) were asked to review the performance of the groundwater recovery and treatment system and to develop a strategy for cost effectively expediting remediation of the site, as well as allowing for the termination of the NPDES-DGW permit.

GEOLOGY AND HYDROGEOLOGY

The unconsolidated sediments in the area of the site are comprised primarily of Pleistocene age sands and gravels of the Atlantic Coastal Plain Physiographic Province. As shown on the generalized geologic cross-section (Figure 2), the unconsolidated material at the site consists of poorly to well sorted, fine to very coarse sand and gravel with only trace amounts of silt and clay. The depth to groundwater averages 8.5 feet below grade, but has fluctuated 2 to 3 feet based on precipitation patterns. These significant fluctuations in groundwater elevations have resulted in the formation of a 5 feet thick "smear zone" of heptane extending above and below the water table. Groundwater flow at the site has been determined to be to the south-southeast at an average gradient of 0.004 ft/ft. Formation permeability values averaged 12.4 ft/day, which is consistent with the type of unconsolidated sediments identified at the site.

FORMER SYSTEM EVALUATION

The former system was evaluated to understand the operating efficiency of the existing pump and treat system. A review of the system data indicated the persistent

presence of separate phase heptane and low product recovery rates at the oil/water separator. Also, the system was no longer capable of maintaining hydraulic control of the dissolved and separate phase plumes. The continued operation of the former system at its operating efficiency would have allowed contamination to migrate off-site, resulting in additional costs associated with impacting the value of the adjoining property. Additional shortcomings of the treatment system included inefficiency and increased maintenance of the recovery wells, oil/water separator and air stripper due to iron and biological fouling, continuous management of the state discharge permit, and projections of over 20 years to achieve cleanup.

In addition, the geology and contaminants of concern were evaluated to determine if pump and treat was the most appropriate technology for cleanup. The project's primary remediation challenges consisted of floating separate phase heptane. As a result of the seasonal rise and fall of groundwater, the separate phase product created a "smear zone" of adsorbed heptane both above and below the water table. The site's fairly uniform grain sizes in the release area also added to the difficulty in removing the contamination through groundwater recovery due to strong capillary forces. The distribution, size, and orientation of soil particles created strong capillary forces that bound the free heptane both in the saturated and unsaturated soils. Furthermore, the adsorbed heptane retained in the unsaturated and saturated soils were not addressed by the pump and treat system.

REMEDIATION ALTERNATIVES

In situ air treatment technologies have been proven to be effective methods of removing VOCs from both the dissolved and adsorbed phases. Air sparging (AS) utilizes the principle of mass transfer by which compounds possessing high vapor pressures partition, or transfer, from the liquid phase (dissolved or adsorbed) into the vapor phase. Air is injected into the saturated portion of the formation using either a compressor or rotary lobe blower. As the air bubbles migrate horizontally and vertically away from the injection well through the zone of contamination, VOCs present in the groundwater partition into the bubbles. The bubbles migrate upward to the vadose zone where vapor phase VOCs are collected by a soil vapor extraction (SVE) system. Soil vapor extraction involves drawing air through unsaturated soils to remove adsorbed VOCs. Compounds that have a high vapor pressure would be "stripped" from the surface of the soil particles and migrate through the soil to an extraction point.

A second mechanism influencing the fate of the compound of concern is the enhancement of biodegradation due to the increase in oxygen in both the saturated and vadose zones. Generally, the primary factor that limits the aerobic biological degradation of hydrocarbons in the subsurface is the availability of oxygen. However, air sparging and soil vapor extraction promote natural biological degradation of many hydrocarbon compounds due to the increased available oxygen content in the saturated and unsaturated zones. Due to its ability to address the dissolved and adsorbed heptane (both above and below the water table) through physical removal and enhanced biological degradation, AS/SVE were determined to be the most cost-effective and expeditious methods of achieving project remedial goals.

REMEDIATION SYSTEM DESIGN

SECOR installed an AS/SVE pilot test system and conducted a series of tests to verify the applicability of the technologies to site conditions, and to facilitate and optimize system design and cost estimation. The SVE pilot test conducted at an air flow rate of 50 cubic feet per minute (cfm) and a vacuum of 29 inches of water (i.w.) resulted in measurable effects up to 80 feet from the extraction well, with a VOC removal rate of 4,080 parts per million by volume (ppmv) or 2.9 lbs/hour; heptane comprised 99% of the VOCs detected in the SVE air stream. However, due to the low vacuum measured at this distance (0.05 i.w.), the effective radius of influence was conservatively considered to be approximately 50 feet. When the air sparging component was added to the pilot test (17 cfm at 7 psi), extracted VOC concentrations (99% heptane) nearly doubled and increased to 7,920 ppmv (4.6 lbs/hour). Groundwater mounding was observed in wells 80 feet from the sparge point, and increased dissolved oxygen concentrations were also detected in wells up to 60 feet away. Consistent with the SVE test, the effective radius of influence for air sparging was conservatively estimated to be 50 feet.

SECOR designed and installed the AS/SVE system during the Spring and Summer of 1995. The AS/SVE system consists of 25 co-located (i.e., within the same borehole) sparge and vent points. The wells used for the pilot test were incorporated into the final system, for a total of 26 AS/SVE points. In addition, an approximately 135 feet long horizontal SVE recovery line was installed under the Mill Area of the facility to collect VOCs from beneath the building. Each sparge point was installed to a total depth of approximately 20 feet with two feet of 0.020-inch slot PVC screen. The vent points have total depths of approximately eight feet, and are constructed with five feet of 0.020-inch slot PVC screen. All of these points were connected to a centrally located equipment compound. Sparge air is supplied by a 30 hp blower with a capacity to deliver air at 400 scfm @ 10 psi. The vapors are recovered using a 40 hp blower (1500 scfm @ 60 i.w.) and are treated using a natural gas powered thermal oxidizer rated for 1500 scfm. Due to the anticipated high mass removal rates, it was determined that a thermal oxidizer would be the most cost-effective method of off-gas treatment. Although the thermal oxidizer cost $45,000, the unit paid for itself during the first month of operation in which 30,000 pounds of non-methane hydrocarbons were recovered by the SVE system. Treatment of the off-gas with vapor phase carbon would have cost approximately $195,000.

SYSTEM PERFORMANCE (MASS REMOVAL)

Upon procurement of the necessary air permits, the SVE component of the remediation system was started on 6 December 1995. The decision to initially operate the SVE system without AS was based on the results of the pilot tests, which showed VOC concentrations almost doubling when the air sparging component was added to SVE. Due to the presence of separate phase heptane, plus heptane's relatively high vapor pressure, it was expected that high concentrations would be extracted from the subsurface when the SVE system was first started. To optimize the performance of the thermal oxidizer and to avoid driving vapor VOCs outside of the influence of the SVE, the SVE system was initially operated without the AS component.

During the first month of operation, mass removal rates averaged 30 lbs/hr, and required that dilution air be added to the influent air stream to keep the thermal oxidizer from exceeding it's maximum operating temperature. Following

approximately six months of SVE operation, during which time mass removal decreased from 5,800 pounds of non-methane hydrocarbons per week to 350 pounds per week, the air sparging system was started (Figure 4). Mass removal increased to 2,700 pounds during the first week of sparging. As of 28 August 1996, 62,000 pounds of non-methane hydrocarbons have been recovered by the AS/SVE system, which is roughly equivalent to 10,930 gallons of heptane.

Evidence of enhanced biological activity has also been noted within the treatment area. Subsurface conditions have changed from anaerobic to aerobic respiration as evidenced by methane concentrations decreasing from 38,000 ppmv during the initial start-up of the SVE system to 28 ppmv after nine months of operation. In addition, bacteria populations in groundwater are up to three orders of magnitude higher within the treatment area ($4.9x10^4$ to $9.3x10^6$ colony forming units [cfu]/ml) than in background areas (9,000 cfu/ml).

The number of years that the AS/SVE system will have to be operated to achieve remedial goals is estimated to be approximately three years. This estimate is based upon the quantity of heptane believed to have been released (approximately 20,000 gallons), the groundwater monitoring data, and the mass removal rates experienced during the pilot test. Additionally, the time to remediate the impacted areas is based upon conservative estimates of the cumulative mass of heptane which would be removed by the AS/SVE system assuming a first order decay equation for the influent concentration. Two to three years of AS/SVE system operation should also enable the remediation criteria for the site to be met, namely 1) removal of separate phase heptane, and 2) the reduction of heptane concentrations in soil to below 1,000 parts per million.

COST BENEFITS

A cost analysis was conducted on the existing pump and treat (P&T) system as compared to the proposed AS/SVE system. The comparison costs for the P&T system included improvements to provide better hydraulic capture over a more extensive plume and associated increased operation and maintenance (O&M) costs. The costs included five to six additional recovery wells, a new treatment system, larger re-injection gallery and modifications to the discharge to groundwater permit to allow a larger volume of effluent. In addition, the O&M for the system was projected out to 22 years based on mass removal calculations. The estimated net present value costs for the improved P&T system totaled approximately $1.13 million that included $200,000 for capital improvements. Costs associated with the AS/SVE system included feasibility studies, pilot studies, engineering design, system installation and O&M. The estimated net present value expenses for the proposed system were $375,000. The costs were computed by projecting a duration of three years based on mass removal estimates from the pilot test results. Comparing the two system's projected cleanup costs showed the AS/SVE would save the facility approximately $755,000.

To insure that the facility achieves the estimated savings, a tracking system was developed to monitor the remediation system's progress versus budget. Figure 5 compares a first order decay curve to actual mass removal data collected from the system. The tracking chart also monitors the targeted budget compared to actual expenditures. The overall graph shows the project is progressing on budget and slightly ahead of the estimated cleanup time goal of three years.

CONCLUSIONS

Following an evaluation of site conditions and the performance of the existing pump and treat system, TBS and *SECOR* recommended an alternative remediation approach. Air sparging and soil vapor extraction were selected due to the ability of these technologies to cost effectively and expeditiously remediate soil and groundwater impacted by adsorbed, dissolved, and separate phase heptane. The performance data collected to date indicate that the site will be remediated in approximately three years, as opposed to the 22 years projected for the pump and treat system.

The cost savings achieved on this project support periodic review of existing remediation system performance to determine 1) operating efficiency; 2) most appropriate technology for current site and regulatory conditions; 3) the need for system improvements; and, 4) whether other technologies should be applied in conjunction with or independently of the existing system to reduce the cleanup costs. The evaluation of an existing system can be a simple diagnostic evaluation of how the system is operating as compared to the original design projections, or can be as extensive as a detailed cost and performance analysis in comparison with other technologies. In an environment of cost reductions through better management, tools such as a tracking system to monitor a project's budget and progress allows a project manager to understand changes in project status and react appropriately.

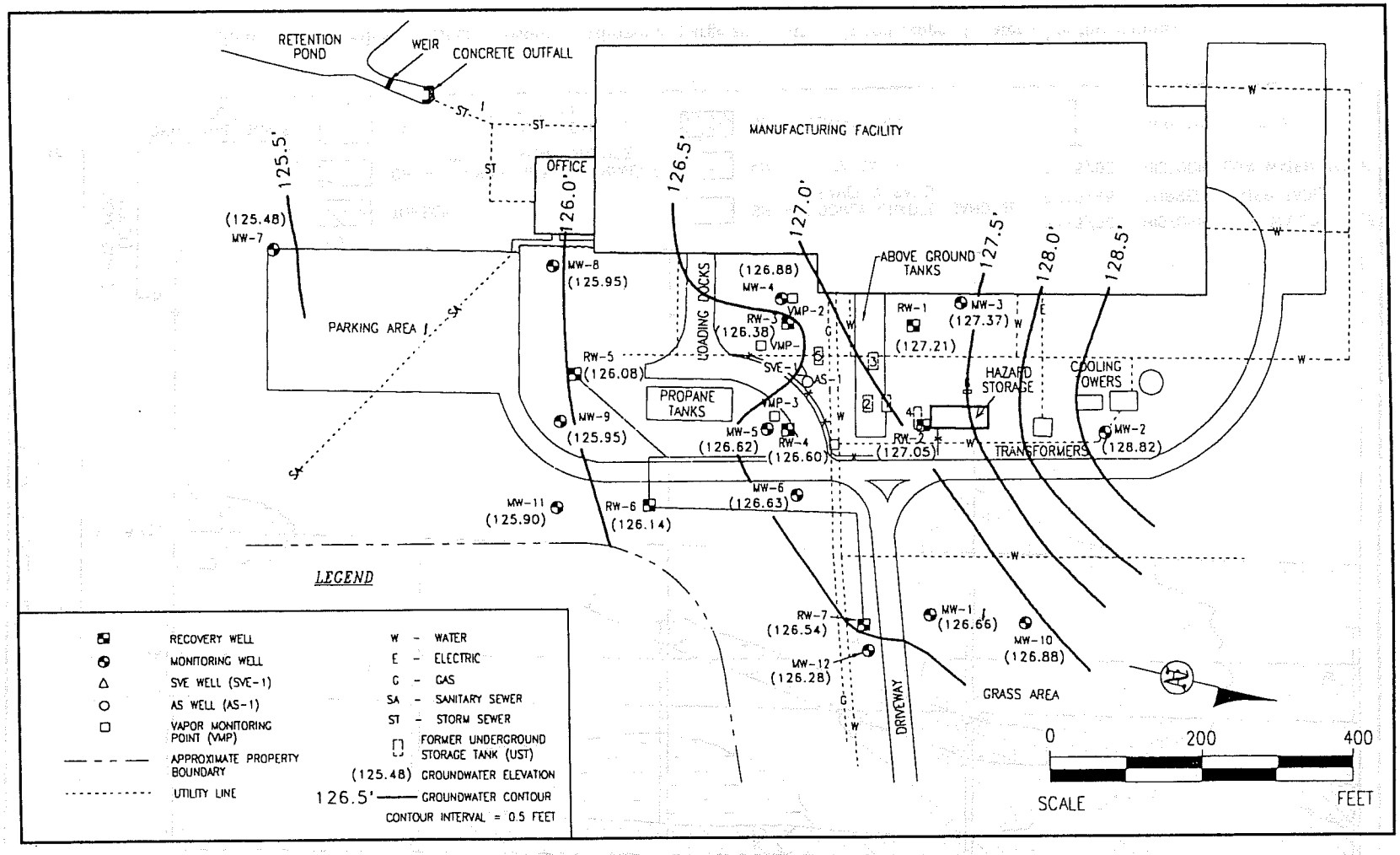

Figure 1. Site plan showing well locations, former underground storage tanks, and groundwater elevation contours.

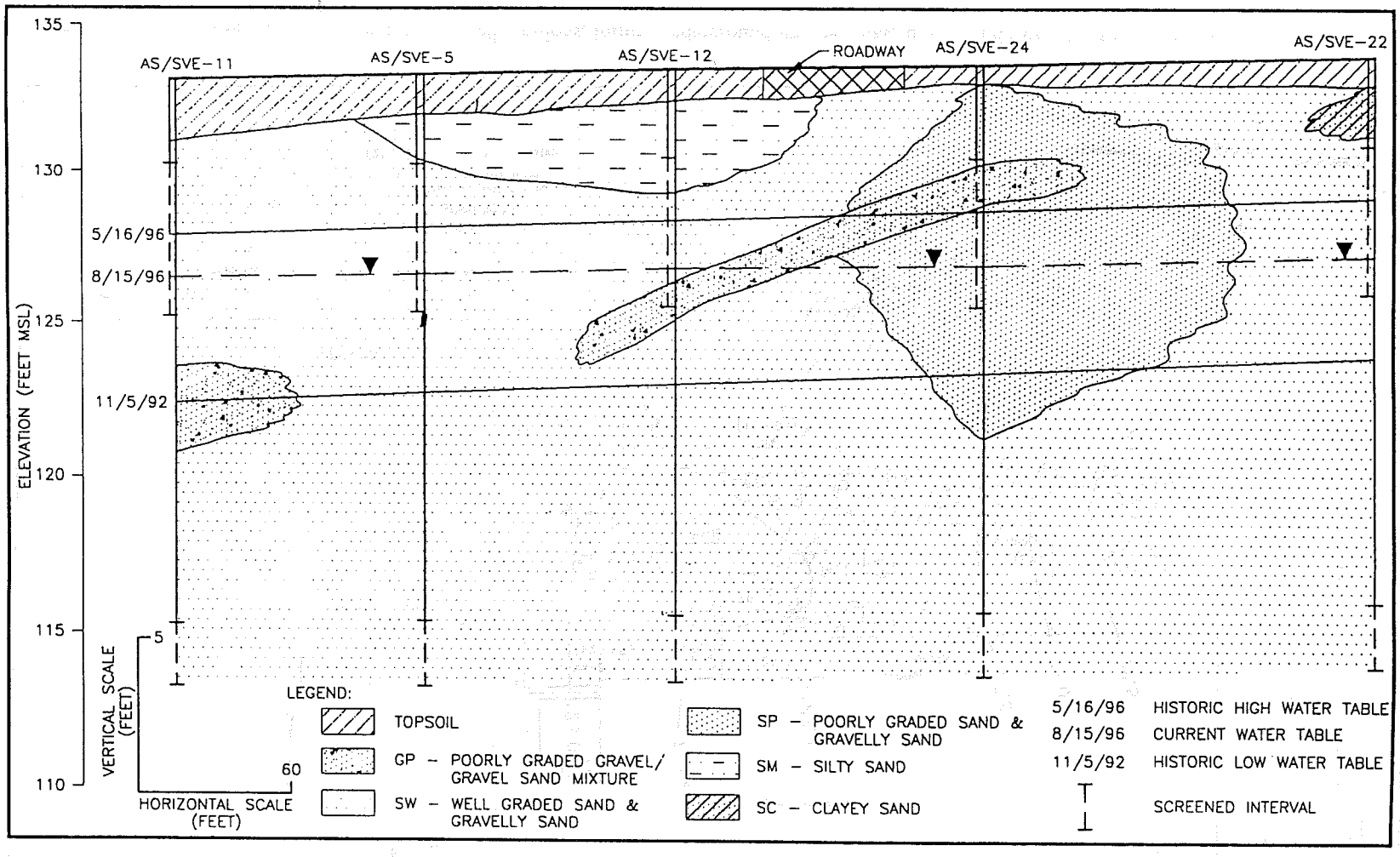

Figure 2. Generalized geologic cross-sectionshowing sparge and vent wells and range of water table fluctuations.

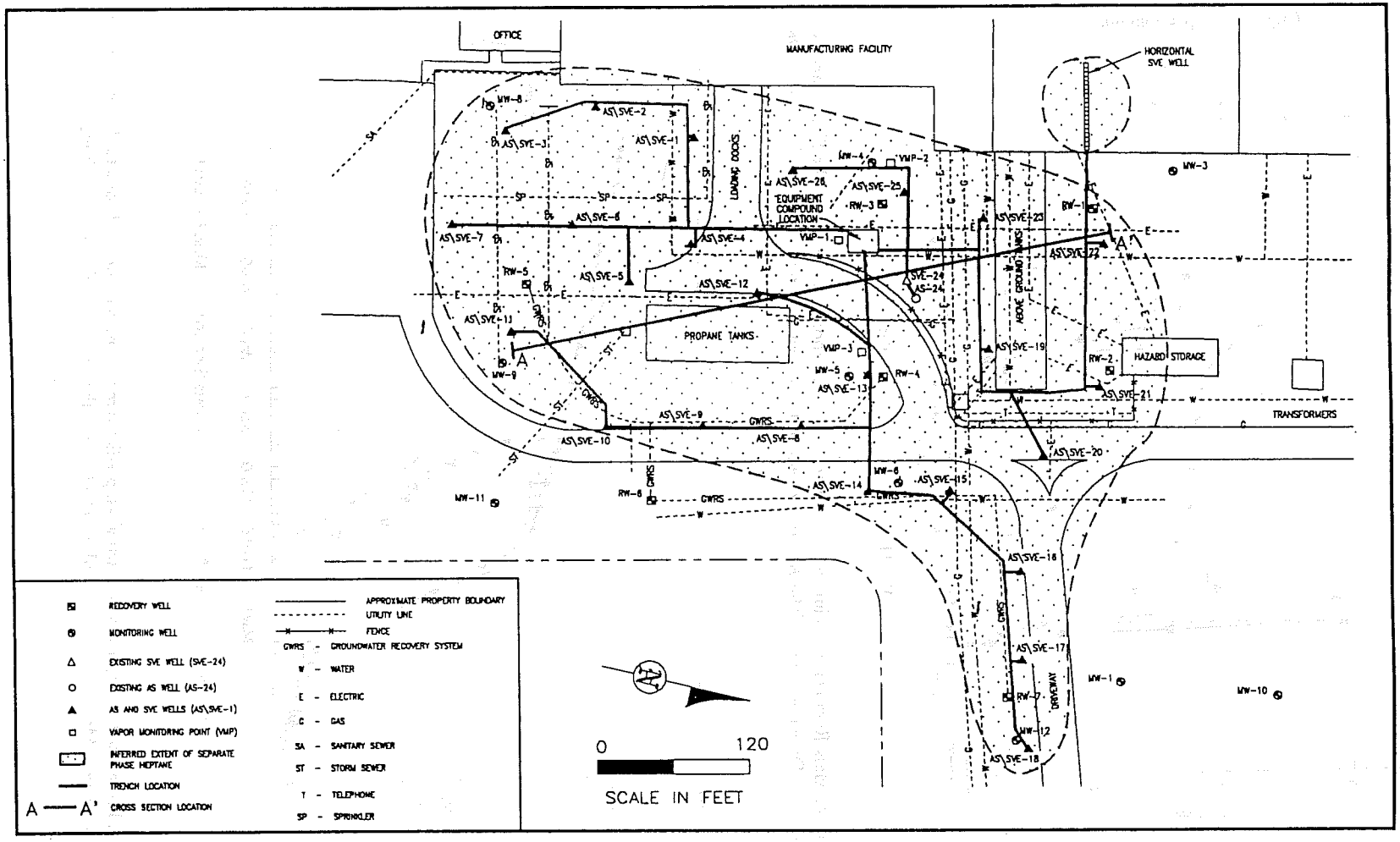

Figure 3. Layout of the air sparge/soil vapor extraction system showing the inferred extent of separate phase heptane.

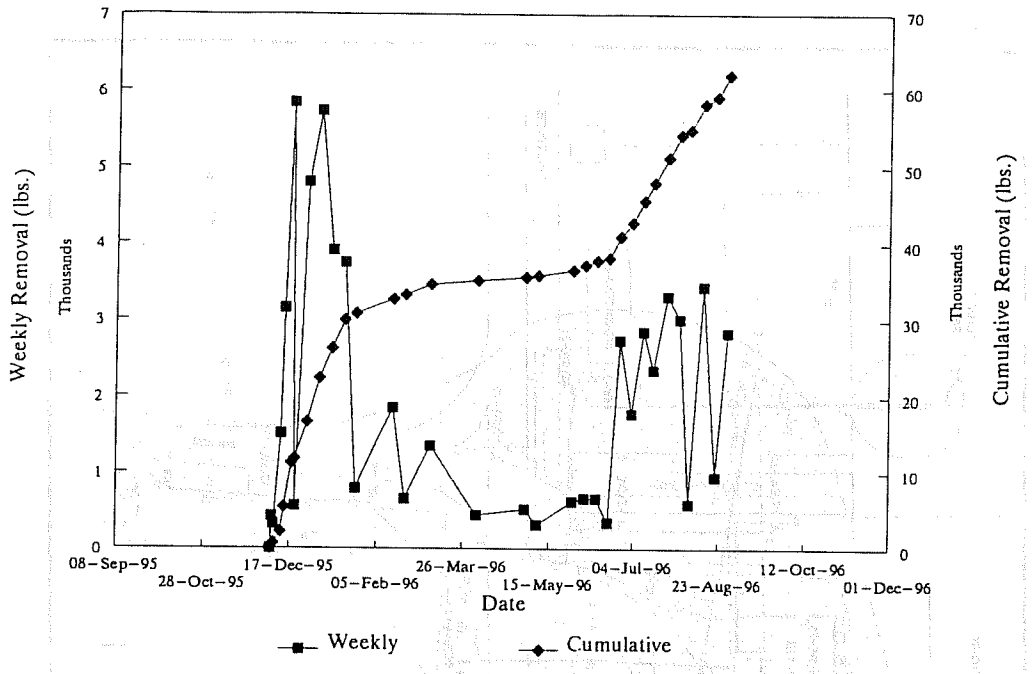

Figure 4. Mass Removal vs. Time for non-methane hydrocarbons (in pounds). The SVE system was started on 6 December 1995. The AS component of the system was not started until 26 June 1996.

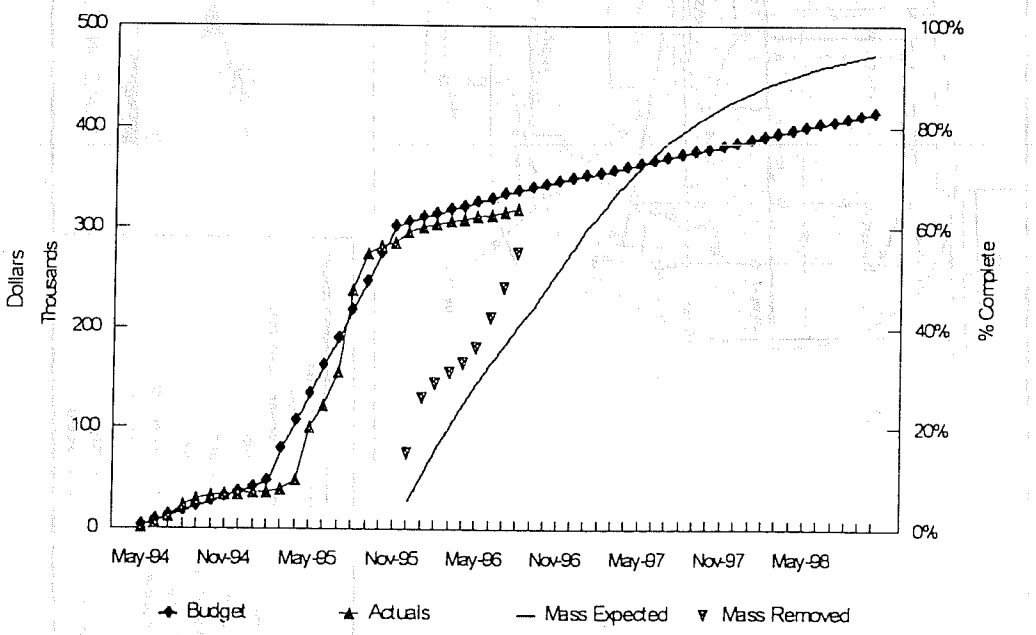

Figure 5. Project status graph showing actual vs. predicted mass removal rates and costs to date vs. original budget estimates. Mass removal is ahead of schedule and the over-all project is under budget.

Pilot Testing and Modeling for the Design of Air-sparging Systems for Remediation of Petroleum Hydrocarbon Contaminated Soil and Ground Water

--Pilot Testing for Effective and Safe Remediation--

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ABSTRACT:

In-situ air sparging (IAS) has become popular for the remediation of petroleum hydrocarbon contaminated soil and ground water. Application of in-situ air sparging beneath a site must be performed carefully but with enough flow and pressure to strip volatiles and stimulate biodegradation. An important aspect of safe operation ensures that sparged gasses are captured with the soil vapor extraction (SVE) component of the system. Sparged gas which escapes the SVE influence, or fugitive vapors, may result in explosive subsurface conditions or odor problems. Pilot testing is performed to obtain data in-situ, via operation of a small scale remediation system and observation of the fluxes in the environment. Calibration of numeric models using the data generated during testing is performed to characterize design considerations specific to the site. Steady-state vacuum development generated by SVE is monitored using a datalogger and pressure transducers. Subsequently, contraction of the steady-state SVE vacuum field is monitored during IAS application. Finally, decay of the vacuum field is monitored following SVE/IAS application. Using analytical techniques such as Hantush-Jacob's curve matching, along with the numerical simulators TOUGH2 and Air3D the interaction between IAS and SVE is modeled. Based on results from pilot test modeling, a system is designed such that fugitive vapors do not occur and effective application of the SVE/IAS is accomplished. Additionally, technologies which treat system exhaust are evaluated based on pilot test data such as flow rate and vapor composition.

INTRODUCTION:

In-situ air-sparging is one of the most dynamic remediation technologies presently employed. Multiphase mixing of air and water in porous media is complex and design of an effective and safe system is not explicit. This paper offers an overview of case study pilot test. The pilot test installation, procedures, results, analysis, and modeling will be discussed.

The case study site is located in the South Valley of Albuquerque, New Mexico approximately one-quarter of a mile from the Rio Grande. The major geologic component of the site is fine to medium sand. Ground water is encountered approximately 12 feet below ground surface (BGS). Petroleum based contamination at the site consists of a mixture of fuels (diesel and gasoline) of which a dissolved-phase plume extends approximately 300 feet in the direction of ground-water flow from beneath the former underground storage tanks (USTs). The plume is approximately 120 feet wide. In addition to this dissolved-phase plume, high concentrations of vapor and adsorbed-phase hydrocarbons are present in the vadose zone. The site surface is comprised of various coverings ranging from asphalt to grass. Subsurface utilities including natural gas, water, sewer, and electricity cross and perimeter the site.

PILOT TEST INSTALLATION:

Selecting an area of the site which is representative of the distribution of contamination and geology is the first step to successful pilot testing. Anomalies such as basement walls or backfilled excavations should be avoided. Pilot testing is generally performed at a dual-completed borehole or reactor nests. The reactor nest installed at the case study site consists of two wells positioned in one borehole which was advanced approximately 10 feet below the water table. The sparge well was positioned at the bottom of the boring with a short (~2-feet long) screen section. The SVE well was positioned in the vadose zone and has 5 feet of screen section. Sand pack was placed around each screen section. Bentonite were injected directly above the sand pack of each well. This design accommodates SVE directly above sparging.

The other subsurface components of the pilot test are the vacuum observation points. Similar to ground-water wells used to monitor drawdown during an aquifer pump test, vacuum observation points are used to monitor the flux of pressure at a specified radial distance from the point of application, the reactor nest. Vacuum observation points are generally constructed from 1-inch diameter steel probe rod with short screen sections. Vacuum observation points

should be installed at different radial directions, distances and depths around the application point.

Five vacuum observation points were installed at the case study site. Two points were installed five feet from the reactor nest, one approximately 5 feet BGS the other 10 feet BGS. Two vacuum observation points were installed 30-feet from the reactor nest in a similar configuration, one approximately 5 feet BGS the other 10 feet BGS. The fifth vacuum observation point was installed 15 feet from the reactor nest approximately 7 feet BGS.

Ground-water monitoring wells screened above the air/water interface and within the observable influence of the reactor nest can be used as a vacuum observation points. Pressure data collected during transient intervals (prior to steady-state) from these converted ground-water monitor wells is often non-interpretable. The relatively low soil-vapor flow rate, fluid compressibility, and the respectively large volume of gas in the monitor well casing offer some explanation for poor transient data from converted monitor wells.

Surface components of the pilot test set-up consist of a power source, SVE and IAS pumps, piping and valves, vapor treatment, data logger and transmitters for flow and pressure, field screening devices, and ancillary equipment. At the case study site, a positive displacement (P/D) blower was used for IAS pumping and a pair of regenerative blowers in parallel was used for application of vacuum at the SVE well. A manifold constructed with 2"-diameter PVC pipe was used to connect the pumps to the respective well heads. These manifolds accommodated installation of differential pressure and flow sensors as well as relief valving used to regulate flow rates. Ports were also installed on each manifold to provide flow stream sampling. Granular activated carbon (GAC) was positioned between the SVE well head and the pump to treat withdrawn soil-vapors. Figure 1 illustrates the pilot test layout at the case study site.

PILOT TEST PROCEDURES:

Pilot testing procedures are divided into two categories; soil vapor pump tests and sparge/vent pump tests. Soil vapor pump test procedures consist of applying vacuum at the SVE well head and monitoring vacuum development at the SVE well head and vacuum observation points. Soil vapor pump tests are performed at three or more different applied vacuums. Vacuum field collapse is recorded between tests.

Sparge/vent pump tests are further divided into the pulse and long term tests. The starting condition for the pulse test is steady-state flow from the SVE well. Once steady-state SVE flow is established, the sparge pump is turned on and flow is developed to approximately half of the SVE flow. IAS is allowed to run for several tens of minutes and is then reduced to zero. Vacuum application at the SVE well remains continuous for several more tens of minutes following the termination of IAS flow. The long term test procedures consist of running a pulse test at steady-state flow for at least 500 minutes.

Flow and vapor composition generated from the well is also recorded during each test. Figure 2 indicates the physical and chemical parameters monitored during pilot testing.

RESULTS:

Results from the tests consist of data plots versus time for the following:

Applied Differential Pressure at the SVE and IAS wells	(IW)
Differential Pressure response at Vacuum Observation Points	(IW)
Flow rate from the SVE well and into the IAS well	(CFM)
Volatile Organic Compounds (VOCs)[1]	(ppm)
Oxygen (O_2) and Carbon Dioxide (CO_2)[1]	(%)
Lower Explosive Limit (LEL)[1]	(%)

[1]-collected from the SVE flow stream

Soil-vapor samples were collected during each test and submitted to an environmental analytical laboratory for determination of total petroleum hydrocarbon (TPH) and boiling point fractions (BPs). In addition to TPH and BPs analyses, one of the soil-vapor samples submitted to the laboratory was analyzed for halogeneated and aromatic volatiles via EPA methods 8010/8020 and lead vapor using atomic adsorption. Results from these analyses were used to assess potential vapor treatment technology.

The charts on Figure 3 depict differential pressure (vacuum) responses observed at the case study site during soil vapor pump tests. Flow rates from the SVE well varied between approximately 45 CFM and 60 CFM. Three soil vapor pump tests were executed at constant vacuums of approximately 3 IW, 5 IW, and 7 IW. Figure 4 charts depict differential pressure (vacuum and positive pressure) observed during the sparge/vent pulse test. Initial conditions of this test consist of steady-state flow of approximately 52 CFM at 5 IW from the SVE well. The sparging is initiated and developed to approximately 18 CFM at 4.5 pounds per

square inch (psi). Vacuum in the vadose zone is observed to contract and stabilize at a lower level as constant sparge flow is established.

PILOT TEST ANALYSIS AND MODELING:

Data from vacuum observation points collected during the soil vapor pump tests are analyzed using standard aquifer pump test curve-matching techniques such as Hantush-Jacob. The method is modified to account for vapor-phase fluid. A basic understanding of the site-specific geology and the results from curve-matching analyses are then used for a starting point to set-up the numerical model Air3D.

Pumping vapor from the vadose zone can be simulated using Air3D, a finite difference flow model. Steady-state flows and pressures observed at the soil vapor pump tests are used to calibrate the model and refine the parameter estimates. In this manner, the vadose zone can be characterized for design of a soil vapor extraction system.

Data from vacuum observation points collected during the pulse tests are analyzed based on the results from the Air3D model described above. Pulse test results indicate that the radial intensity of the vacuum field in the vadose zone recedes due to sparge flow breakthrough into the capillary fringe. This effect can be simulated using Air3D. The model grid is constructed in a 2-dimensional fashion, a single cell wide but otherwise the same as the 3D model set-up described above (a cross-sectional slice through the reactor nest). A block of no-flow cells is added at the bottom the 2D grid to simulate the 10 feet of the aquifer. A triangle is deleted from the no flow cells. The tip of the triangle wedge is positioned at the bottom of the sparge well and the base of the triangle is aligned with the top boundary of no-flow cells which represents the aquifer surface. This wedge defines the boundaries of the zone of desaturation generated via sparging. Injection and extraction wells are positioned in the model. The vacuum applied at the model SVE well is set equal to the vacuum applied during the pulse test at equilibrated sparge flow. The pressure applied at the model sparge well is set equal to the difference between the pressure applied during the pulse test at equilibrated sparge flow and the head of water above the sparge point screen. This is the break-out or capillary pressure in the formation.

Pressure values at nodes in the simulation which correspond to the locations of the vacuum observation points are compared with the data from the pulse test. Calibration is achieved by altering the width of the base of the triangle which represents the zone of desaturation. Model results are depicted in Figure 5.

Since the Air3D simulation described above does not take into account the true mechanisms controlling sparge flow, the results generated are subject to substantial interpretation, especially concerning the shape and pressures within the zone of desaturation. Numerically simulating a multiphase fluid flow such as air-sparging requires a model which accounts for fluid properties and relative media terms outside the capabilities of Air3D. These parameters include the following:

$f(k_{r,air}), f(k_{r,water})$;	relative permeability functions for each fluid
$f(N_c)$;	capillary pressure function
m and α;	van Genuchten fitting parameters
λ and M;	the mobility function and mobility ratio

The TOUGH2 simulator was used to verify the shape and pressures of the zone of desaturation. In addition, valuable insight into the development of a zone of desaturation was achieved. The sequence of plots in Figure 6 depicts the development of a steady-state zone of desaturation as simulated using TOUGH2. Model results indicate a reasonable relationship. The zone of desaturation roughly resembles a parabolic cone approximately 35 feet in diameter at the aquifer surface.

CONCLUSIONS:

Based on the results from the modeling described above, reactor nest spacing and distribution is determined for the remediation system. Expected flow rates and pressures are estimated based on the system layout and pilot test results. Pump types and sizes are selected based on the flow rate and pressure estimates. Vapor composition data gathered during the pilot test is used to model the expected atmospheric loading from system exhaust. If necessary, a vapor treatment system is designed based on expected flow rates and vapor composition.

Model results give valuable insight into the direction and intensity of flow in the vadose zone. Notably, SVE intensity diminishes due to sparge flow breakthrough at the aquifer surface. The path of gas flow alters such that sparged gasses are captured at the SVE well. This can be observed in the SVE model results by the more spherical vacuum bands around the SVE well with sparging depicted in Figure 5. These results indicate that pulsed sparging operations may enhance SVE performance by intensifying and redirecting SVE flow during IAS downtime.

Utilization of pilot testing and modeling will optimize remedial designs while still ensuring safe operation. Specifically, in-situ air sparging system designers should consider the effect sparging has on the vacuum field. Since the vacuum field shrinks due to sparging, designers should not base reactor nest spacing on soil vapor pump test analyses alone. Sparge/vent pulse and long-term test analyses will yield the necessary results to properly characterize a site for in-situ air sparging design.

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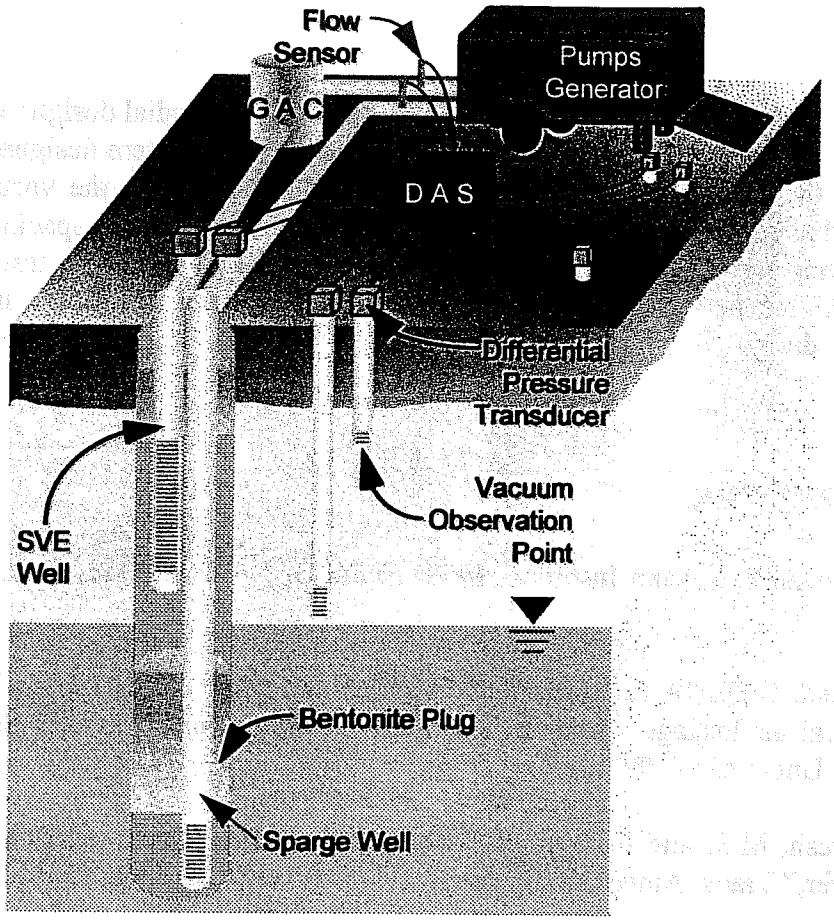


Figure 1: Pilot Test Set-up

SAMPLE LOCATION	VOC (ppm)	CO_2 (%)	O_2 (%)	LEL (%)	ΔP (IW)	Q (CFM)	DO (ppm)
Sparge Well Head			✋		≈	≈	✋
SVE Well Head	✋	✋	✋	✋	≈	≈	
Post-Treatment SVE	✋			✋	✋		
Vacuum Obs. Pts.	✋	✋	✋	✋	≈		
Ground-water Well							✋

✋ - hand sampled ≈ - electronic logger

Figure 2: Physical and Chemical Properties Monitored

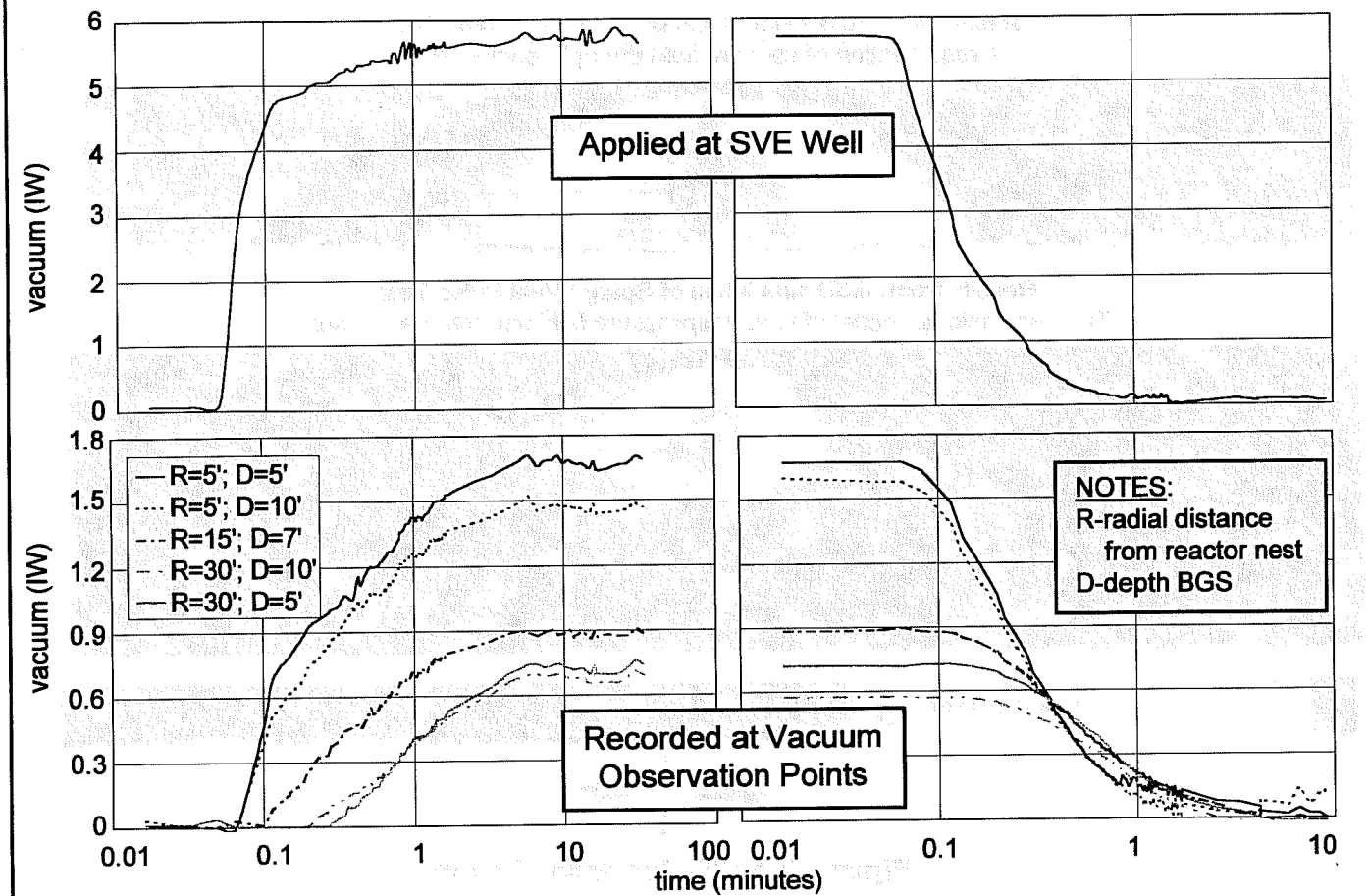


Figure 3: Vacuum Pump Test Pressure Response Results

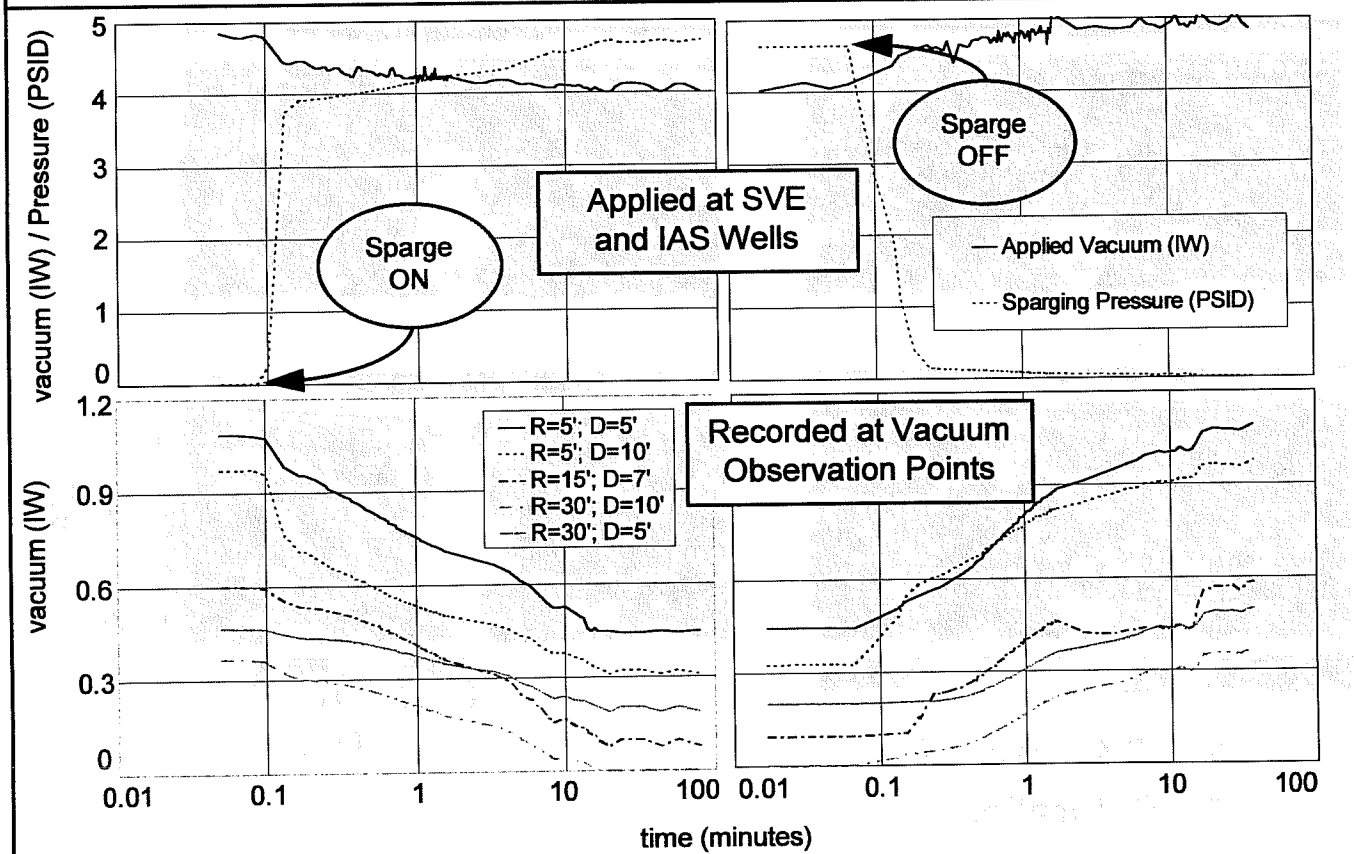


Figure 4: Sparge/Vent Pulse Test Differential Pressure Results

Results from Air3D simulation of Soil Vapor Pump Test.
Cross-section of vacuum field through reactor nest.

Results from Air3D simulation of Sparge Vent Pulse Test.
Two-dimensional model of vacuum/pressure field through reactor nest

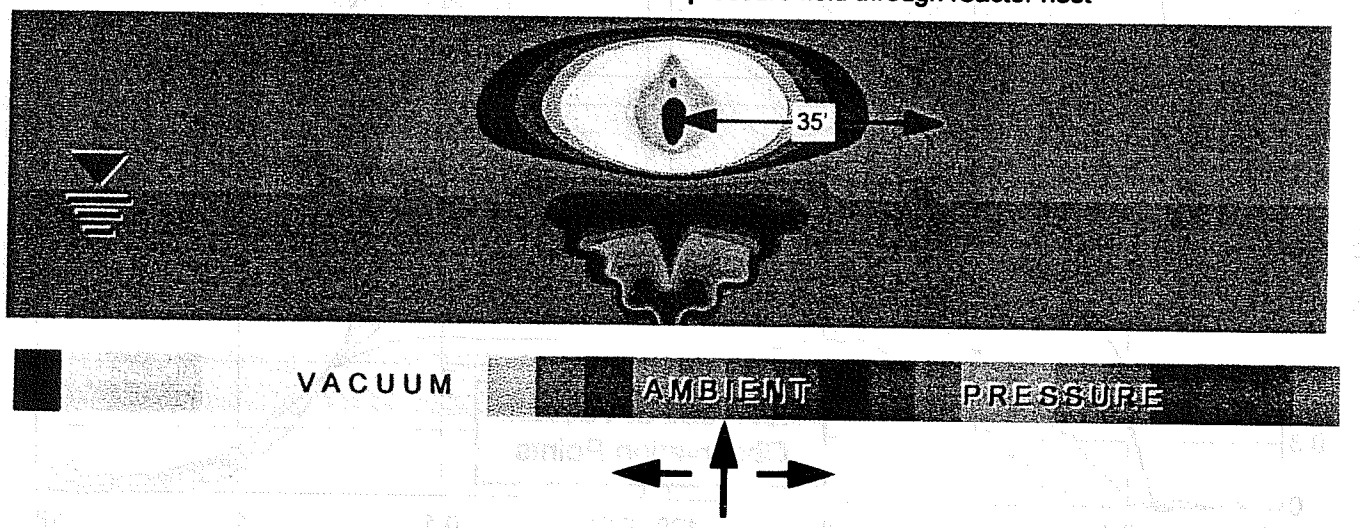


Figure 5: Air3D Simulation Results

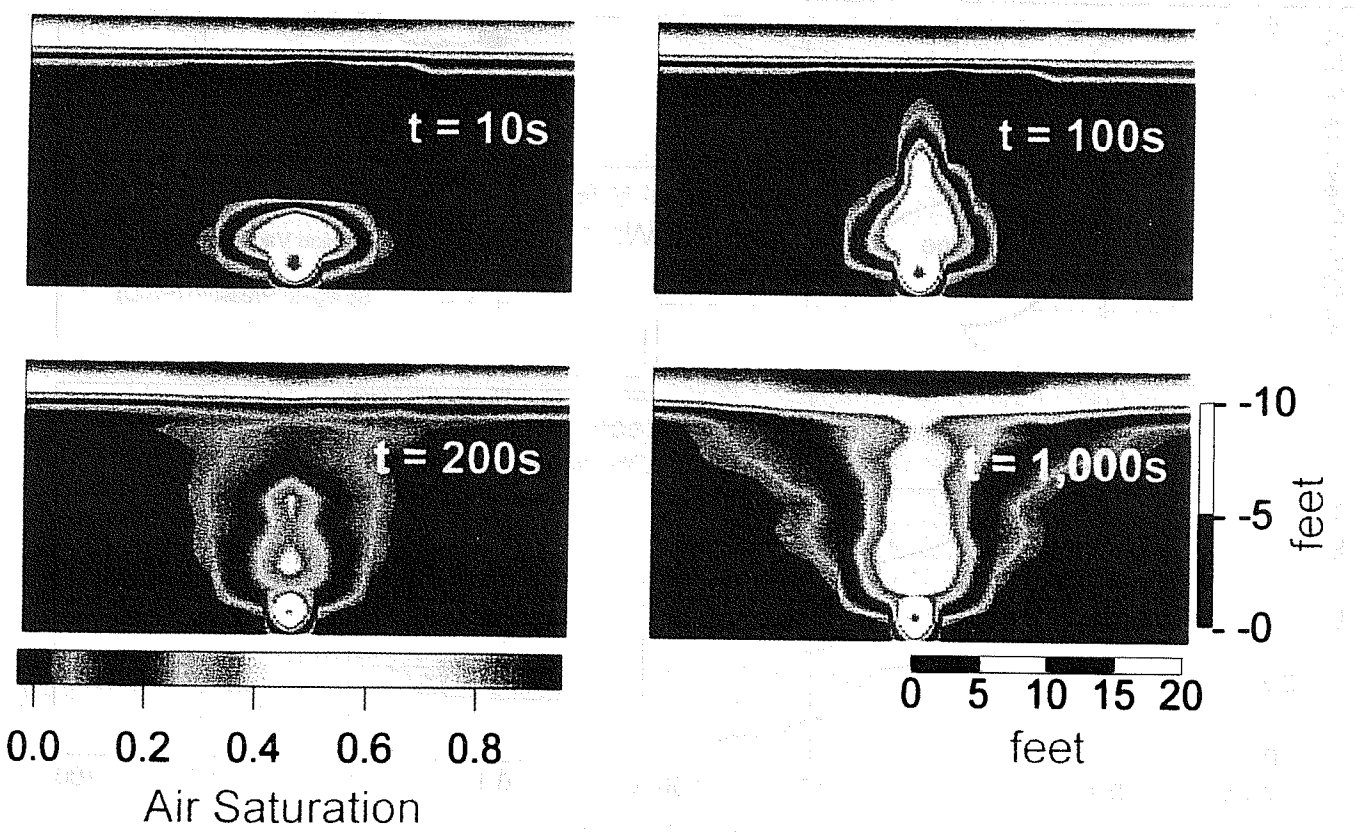
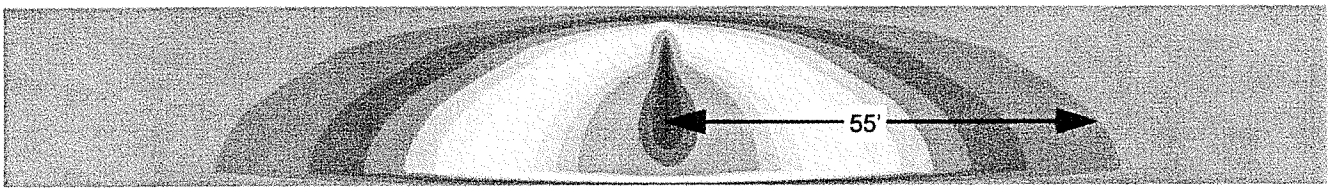
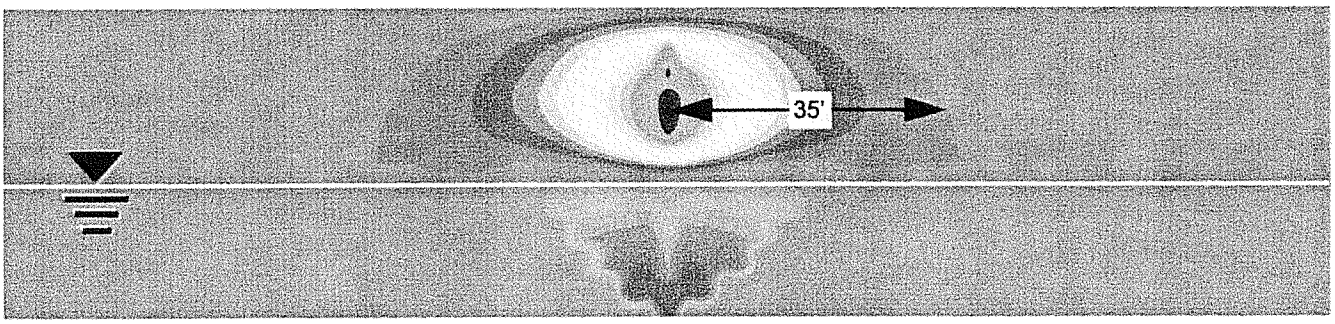


Figure 6: TOUGH2 Simulation Results

Results from Air3D simulation of Soil Vapor Pump Test.
Cross-section of vacuum field through reactor nest.



Results from Air3D simulation of Sparge Vent Pulse Test.
Two-dimensional model of vacuum/pressure field through reactor nest



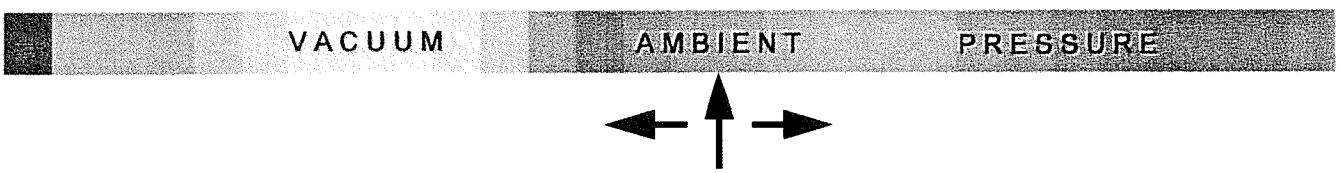


Figure 5: Air3D Simulation Results

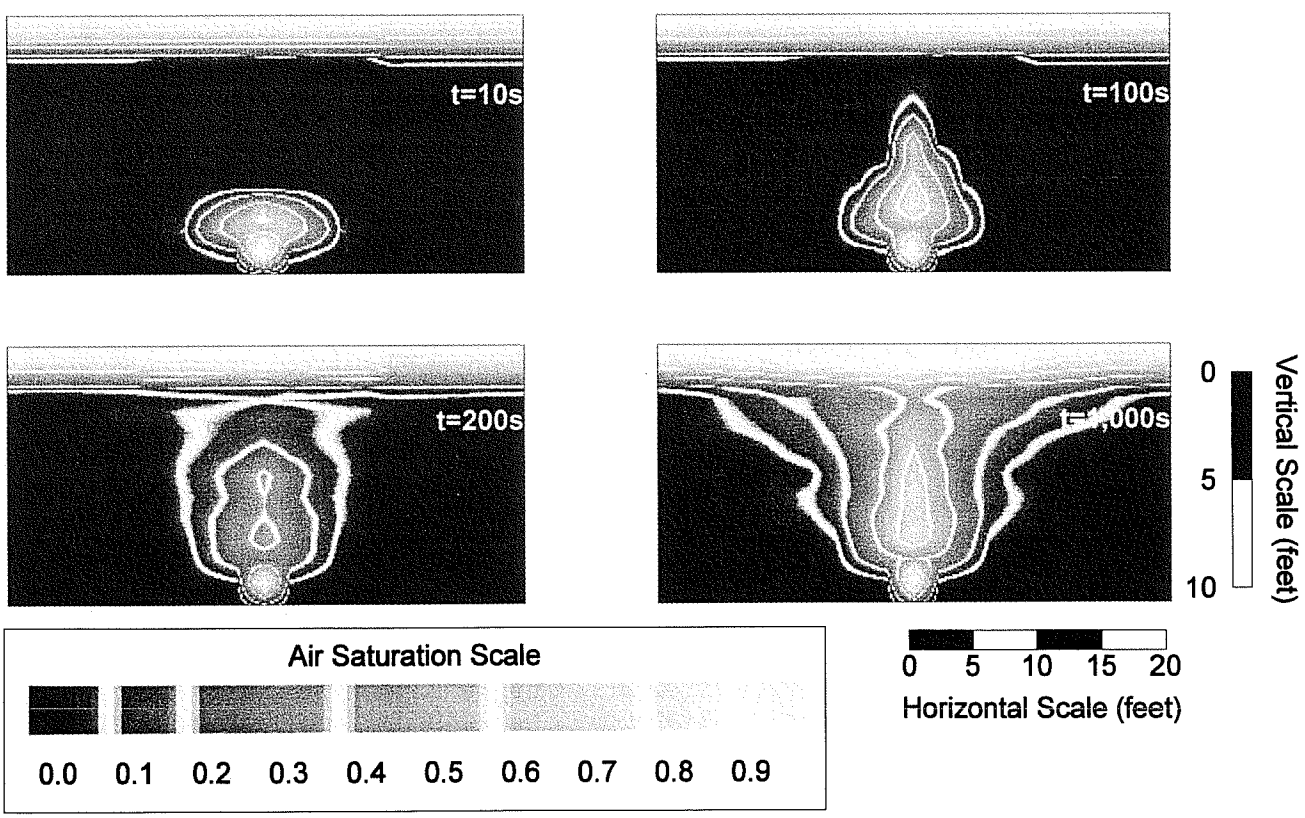
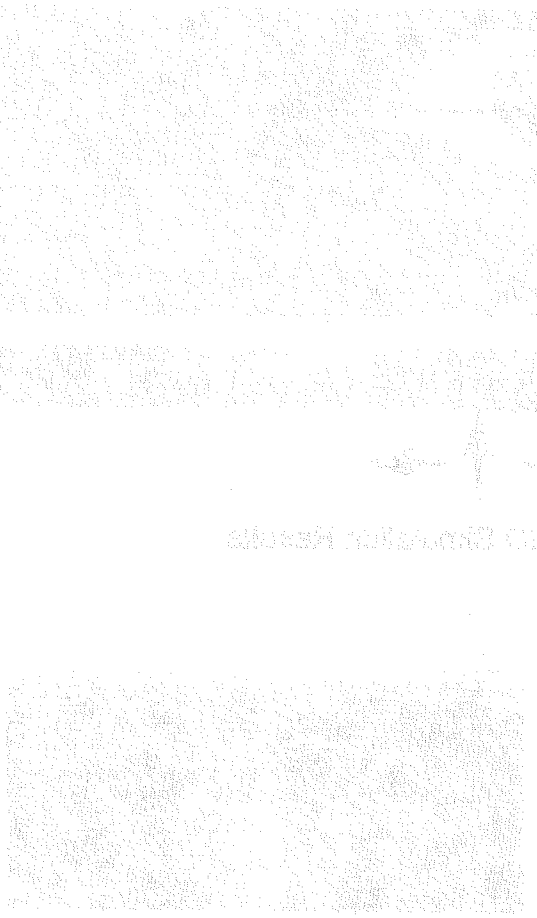
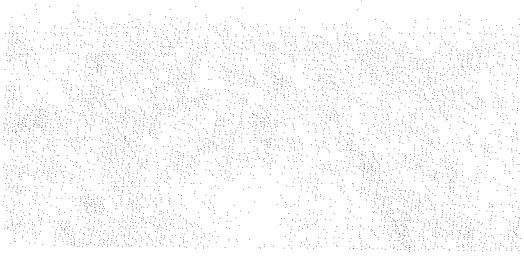
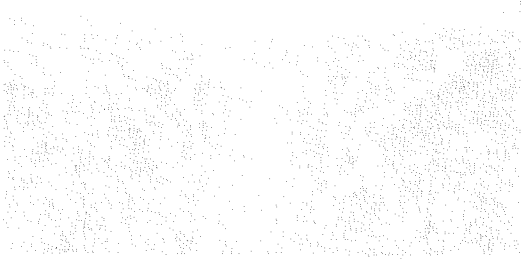
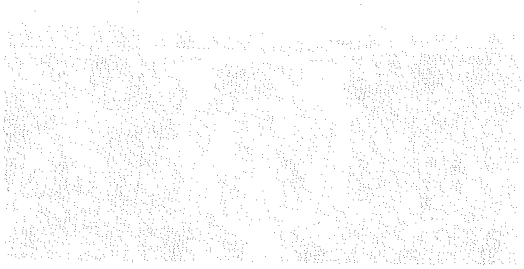


Figure 6: TOUGH2 Simulation Results









Oil Contaminant Removal from Drill Cuttings by Supercritical Extraction

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ABSTRACT

When an offshore oil well is being drilled with an oil based mud, environmental regulations and concerns severely restrict drill cuttings disposal options. This has led a high percentage of drilling contractors to use less effective but environmentally acceptable water based muds. An economically feasible system which uses oil based mud accompanied by acceptable offshore disposal of cuttings is much preferred.

Experimental results of this study indicate that supercritical extraction will reduce the oil based mud contamination of drill cuttings to a value suitable for offshore disposal. Batch pilot plant experiments were conducted using HFC 134a and propane as supercritical extractive solvents. A commercial process design and cost estimate were also prepared. The cost estimate indicates that the supercritical extraction technology is very competitive with current cuttings disposal technologies. This process offers the advantage of allowing the continued use of oil based mud in environmentally sensitive areas - a major benefit for drilling operations.

Continuous extraction through countercurrent contacting is an extremely complicated process, and requires unique equipment. Various commercial process flow schemes are presented taken primarily from the bitumen extraction literature. Air emissions control and solid fines removal are also discussed.Experimental results indicate that supercritical extraction will reduce the oil based mud contamination of drill cuttings to a level that will allow offshore disposal. Pilot plant experiments were conducted using HFC 134a and propane as the extractive solvents. A commercial process design and cost estimate was prepared. The estimate indicates that the supercritical extraction technology is very competitive with current cuttings' disposal technologies. The process offers the advantage of allowing the continued use of oil based mud in environmentally sensitive areas - a major benefit for drilling operations.

INTRODUCTION

A wide range of supercritical extraction processes have been studied over the past decade.Unfortunately, a limited number of processes have been brought to commercialization. The notable exceptions include coffee bean decaffination (12), supercritical water based oxidation of pullutants (10), and the deasphalting of heavy oils (6). In order to be competitive, the supercritical extraction process must have a significant advantage over traditional separation processes. This advantage must off-set the capital cost of high pressure equipment and, in the case of a volatile solvent (such as carbon dioxide) the cost of feed compression. For the extraction of FDA regulated material, carbon dioxide provides the advantage of a non-toxic solvent. For petrochemical applications, the advantages are primarily the ease of solvent recovery. Liquid solvent processes which require a complex distillation system to recover the solvent can be replaced with a supercritical

process which reclaims the solvent by a simple pressure reduction. Supercritical processes which develop the contactor pressure with a pump are obviously preferred over processes which use a compressor. Solvents which have good selectivity and capacity for contaminants and have relatively low critical pressures and temperatures are the most efficient. For the removal of hydrocarbon based contaminants, light hydrocarbons (ethane, propane, butane) readily meet this criteria. Unfortunately, these materials carry significant safety concerns due to their high volatility and explosion potential. The new generation of environmentally friendly HFCs offer some of the benefits of light hydrocarbons while eliminating these safety concerns. The experiments outlined below utilize both propane and HFC 134A to extract oil based drilling mud contamination from drill cuttings. The proposed processing scheme takes advantage of the solvents low critical pressures and temperatures. Both solvent's vapor pressures allow the feed to be pressurized with a centrifugal pump, thus significantly reducing the equipment cost and complexity.

CUTTINGS DISPOSAL

As wells are drilled large amounts of rock cuttings are produced (detailed properties of the rock cuttings used in the test program are given in Table 1). These cuttings come to the surface in a slurry with the drilling mud (Figure 1). The slurry is physically separated through a mesh screen (a shaker table) which reduces the oil content of the slurry to around 15 percent. If an offshore well is being drilled with oil based mud, environmental regulations severely restrict cuttings disposal options. Current disposal approaches involve reinjecting the cuttings into the producing formation (see Figure 2) or transporting the cuttings to shore for incineration or burial. Transporting cuttings to shore from a remote platform is very costly and on-shore disposal regulations are becoming more restrictive. Reinjection requires that a well slot that could be used for production be allocated to waste disposal. In some locations, the platform operator must demonstrate that the reinjection of oil contaminated cuttings will not lead to contamination of ground water near the reinjection well. These factors have led a high percentage of drilling contractors to the use of water based, environmentally acceptable, muds. Unfortunately, water based muds do not perform as well as oil based muds. The reduced lubrication between the formation and the drill string increases the probability that the string will become stuck in the hole. Drill bit penetration rates are also reduced. Both problems can significantly increase drilling costs. Ideally, an economically feasible system which allows the use of oil based mud and the offshore disposal of cuttings would be preferred. The goal of the project outlined below is to develop such a system.

OIL REMOVAL

Oil based muds are paraffinic in nature with a relatively high boiling range (a typical distillation curve is given in Figure 3). This high boiling range makes oil removal from contaminated cuttings difficult. Various approaches have been attempted to remove the oil from the rock; the use of high temperature (4), liquid solvent extraction (5), and soap and water washing (2). All these techniques suffer from safety, complexity, or high energy use problems. A process based on supercritical solvent extraction is a favorable alternative. The patent literature

contains some initial work in the area (1). The current project involved pilot plant testing, commercial design development, and a feasibility level cost estimate. The results indicate that the process is technically sound and economically superior to existing technologies.

PILOT PLANT TEST PROGRAM

In order to prove the process's technical feasibility, a series of pilot plant tests were conducted. The pilot system and typical HFC 134a test conditions are shown in Figure 4. The oil containing cuttings were loaded into a one liter heated stainless steel autoclave. The autoclave was pressurized to supercritical conditions using a positive displacement pump. Once at pressure, the solvent flowed through the agitated contactor, through a pressure reduction regulator, and into a heated flash vessel. Pressure in the flash pot was maintained at a sufficient level to allow the overhead gas to be condensed with cooling water before returning to the pump feed tank. Two solvents, with similar critical properties, were tested: HFC 134a and propane (properties given in Table 2). Propane was an effective solvent, exhibiting satisfactory levels of oil removal. However, concerns about flammability hazards eliminated its consideration for an offshore platform process. Extraction results for propane and HFC 134a are shown in Figure 5 and Figure 6 with test conditions given in Table 3. The pyrolysis GC output (details of analytical procedures are given below) indicates a very high (> 98 percent) removal of the oil contamination. The plot of autoclave content weight loss, for the HFC 134a experiments, given in Figure 7 indicates that for (WHSV * residence time) values greater than 20, similar hydrocarbon removal was obtained. (Note: Weight Hourly Space Velocity is the mass flowrate of the solvent divided by the mass of cuttings and oil initially in the contactor). Variations in the absolute weight loss above 20, are attributed to the nonhomogeneous nature of the contactor feed which was charged from the sample container with a large mortar trowel. For all tests, the feed material was obtained from a North Sea oil based mud drilling operation.

No significant operating problems were experienced during the pilot plant tests. The cuttings tested were very fine and precautions had to be taken to eliminate their transport into a downstream solvent equipment. A fine screen provided adequate protection at the pilot plant scale. Further investigation will be needed to perfect a screen / filter system for the commercial design. The autoclave stirring system was trouble free at the cuttings loading tested. No contactor wall erosion was observed during the tests.

The distillation curve presented in Figure 3, was obtained from oil collected in the solvent flash tank during the initial HFC 134a experiment. The simulated distillation test (GC based) used to generate the curve detected no residual solvent in the oil. Also, no appreciable loss of solvent was detected during the course of the experimental program. However, the ultimate quanitation of HFC losses must be determined during larger scale "proof of concept" testing. HFC 134a is an expensive solvent and losses through either absorption into the oil or adsorption onto the cuttings must be minimized in order to obtain favorable economics.

ANALYTICAL PROCEDURE

Pyrolysis gas chromatography was used to determine the level of oil contamination of the drill cuttings. The technique utilizes a two step procedure. The drill cutting sample is heated to 300 C and the vaporized oil is carried into a gas chromatograph by a helium carrier stream.A cryogenic trap is used to optimize the gas chromatograph resolution.For the current test, a 30 meter capillary column coated with DB-5 cross-linked methyl silicone phase was used. A temperature ramp program ranging from -20C to 320 C was run to elute the sample.

COMMERCIAL DESIGN PREPARATION

The commercial design was based on results from the pilot plant test program. Design premises are given in Table 4. A batch system was selected with circulation of the HFC solvent through a stirred contactor (Figure 8).The design rock / oil slurry rate was based on a typical average drill bit penetration rate (rock cuttings generation rate).The contactors were designed to contain 50 percent feed and 50 percent HFC solvent. The solvent flash vessel conditions were fixed to allow a seawater cooled HFC condenser. A pump supplied feed to the contactors. Two contactor vessels were used, one vessel will be loaded or unloaded while the other vessel is "on-line". Heat will be provided to the process by low level waste heat available on the platform or by a dedicated low pressure (40 psig) steam system. An augur system will transfer the cuttings from the primary separating device (the shale shaker) to the extraction system. Solids will be discharged from the contactor at the end of the treatment cycle by air pressure or gravity drain. HFC released during contactor depressurization will be recovered by a small vapor recovery system. The HFC inventory on the platform will be minimized with make-up requirements being maintained at an on-shore facility and transported to the platform by supply ship.

COST ESTIMATE RESULTS

The cost estimate was prepared using costing algorithms available in the Aspen Plus process simulator. The feasibility grade (+35% to -15%) estimate results are given in Table 5.Onshore cost results obtained from Aspen Plus (Aspentech, Cambridge, MA) were scaled by a factor of three to reflect offshore construction and installation. It is anticipated that the system could be built in modules thus simplifying offshore installation. Initial calculations indicate that the weight and space requirements of the supercritical extraction system will not exceed those of a traditional cuttings reinjection system. The installed cost of $ 4.8 million competes very favorably with data available for alternative technologies. For comparison the literature (7) indicates that a reinjection system for a 20 well program would cost $ 9.6 million. Costs for onshore processing, advanced biodegradable oil-based muds, and water based muds were given as $ 18, $ 19.5, and $ 39 million respectively.

CONCLUSIONS AND FUTURE WORK

The experimental results and cost estimate indicate the process has technical and economic potential. Additional experimental work is need to prove the concept and optimize the process design before installation on an offshore rig

can be considered. A semi-works scale unit which takes feed from an operating rig shale shaker will be required to validated the process. The solids transport system needs to be thoroughly addressed. Scale-up data is need for the contactor system and the solvent circulation rate per pound of cuttings must be optimized. This scale-up might best be accomplished through a cooperative effort involving several operating companies.

Bio-toxicity limits are currently being incorporated into offshore environmental regulations. Any oil removal process must produce cuttings which are not toxic to test organisms. Therefore, at some point in the process development, a series of toxicity tests must be conducted on the cuttings yielded from the supercritical extraction unit. The diversity of organisms used in bio-toxicity testing worldwide makes this testing step complicated an expensive.

The construction of a fundamental model of the extraction process would be of great benefit. Figure 9 gives a overview of the contacting process. The non-steady state process is extremely complicated. The mass transfer mechanism changes radically as the solvent removes the oil from the contactor. The model must have properties of both a supercritical fluid / liquid absorption process and a supercritical fluid / solute desorption process. Equations to describe the physics of both situations are well known (9), (11), (3).However, the simultaneous solution of the applicable equations and prediction of mechanism transition points will be a very challenging mathematical and engineering problem.

Solids Handling

The solids handling during solvent extractions is extremely complicated and requires unique equipment. Penney and Ulrich (8) have published a review of such equipment which includes several schemes using:

- a sloped vessel containing augers,
- a rod or ball mills,
- a countercurrent moving bed in a vertical vessel,
- a comparted, agitated, vertical vessel,
- a rotary drum mixer followed by countercurrent wash in a series of hydroclones.

The potential advantages and disadvantages of all these are discussed along with selected other schemes. The handling of fluids is also discussed. Figures 9 and 10 of this article present typical solids handling schemes.

Air Emissions

The Penney and Ulrich paper (8) also discusses control of air emissions which become key design aspects, particularly the point sources emissions that occur at the feed to the extractor and at the sand clean-up unit. A method of handling there emissions is shown on Figure 10.An inert gas purge stream is used in-line between the feed auger and the agitated extraction vessel which is then fed to a solvent recover condenser. A gas purge stream is also used prior to the drill cutting disposal exiting from the flash dryer, and recycled back to the same condenser.

Figure 1 Typical Drilling Rig Configuration

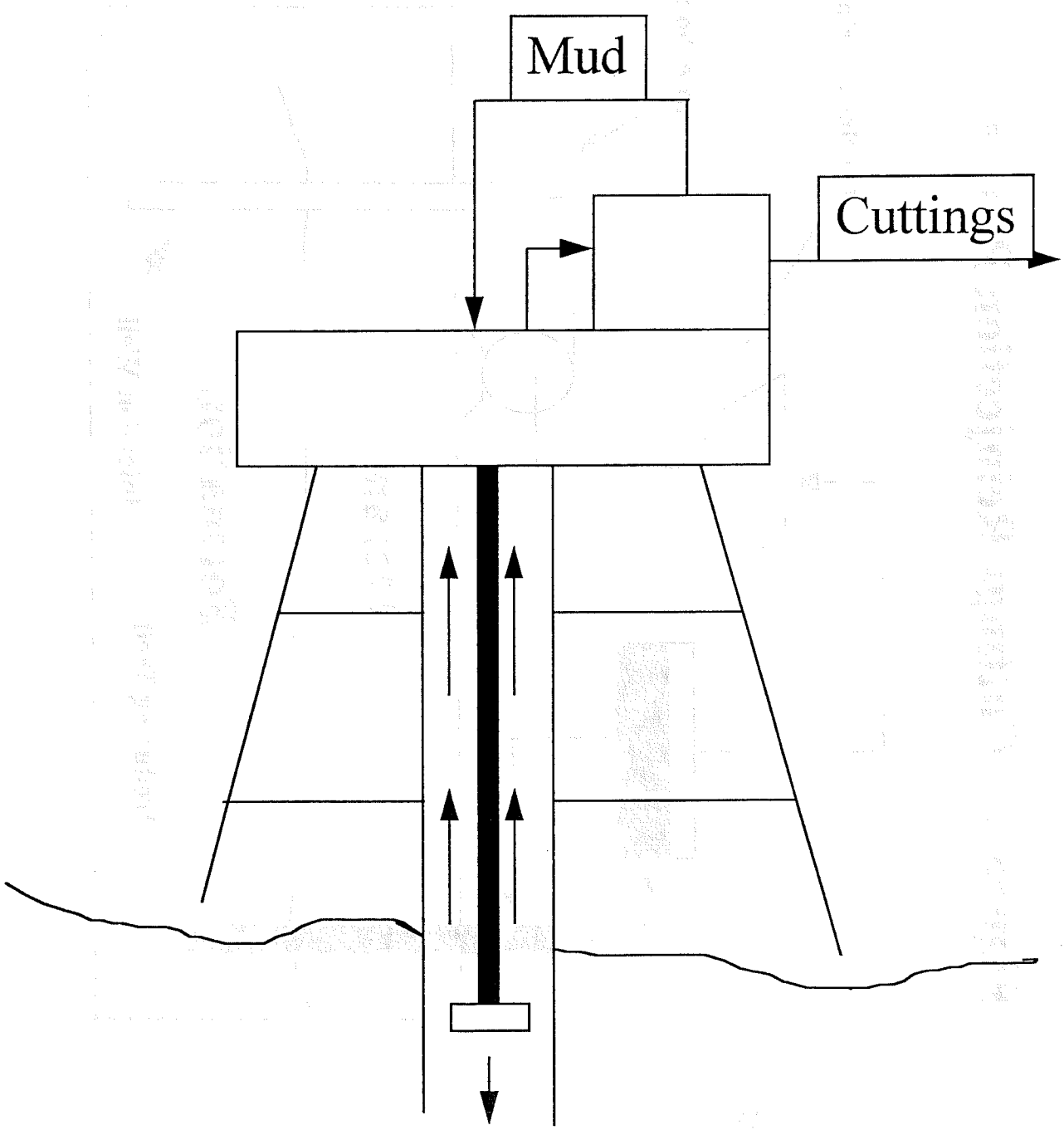


Figure 2 Cuttings Reinjection Process

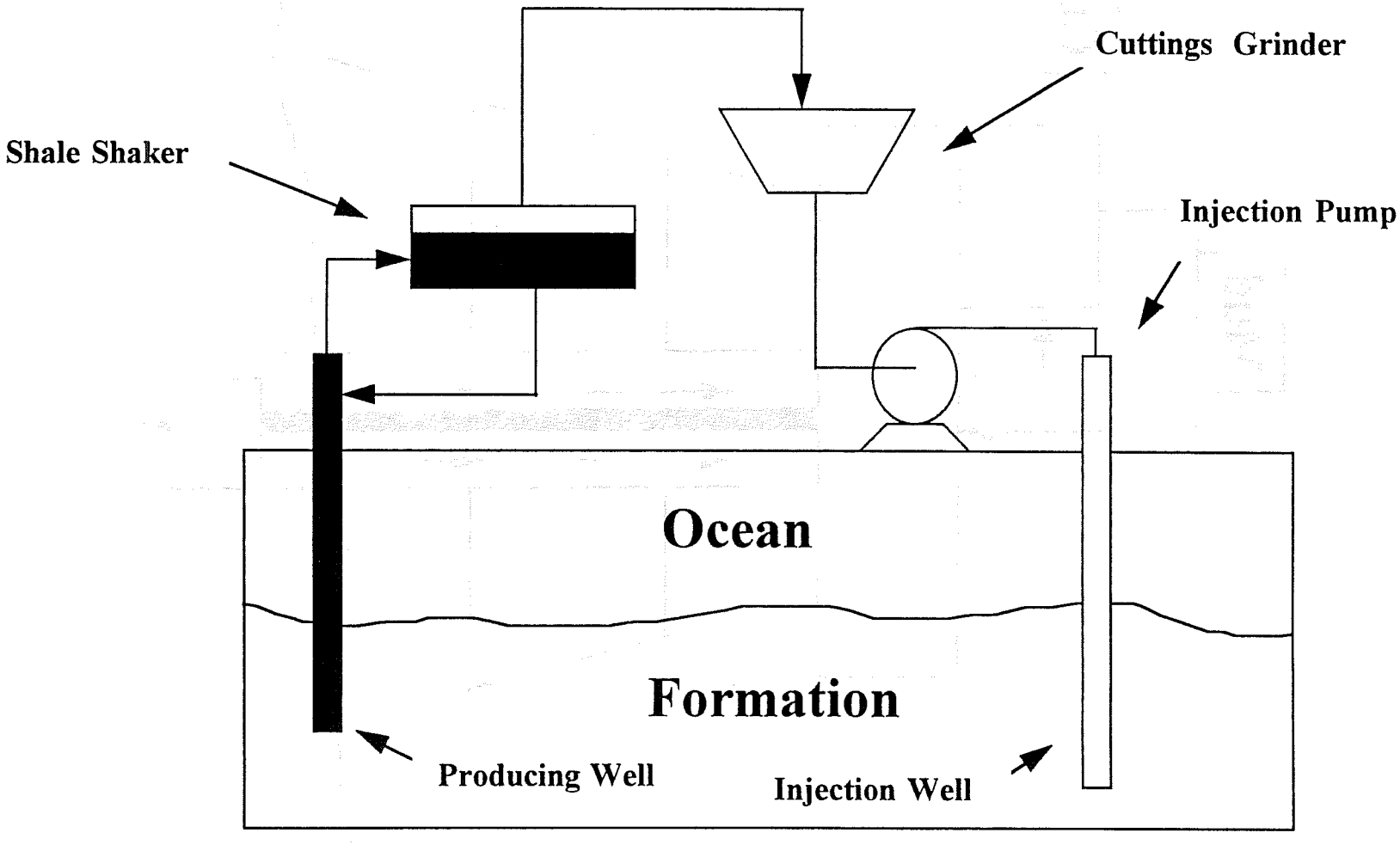


Figure 3 Distillation curve for oil used in oil-based mud. (Obtained from solvent flash tank - Run No. F1)

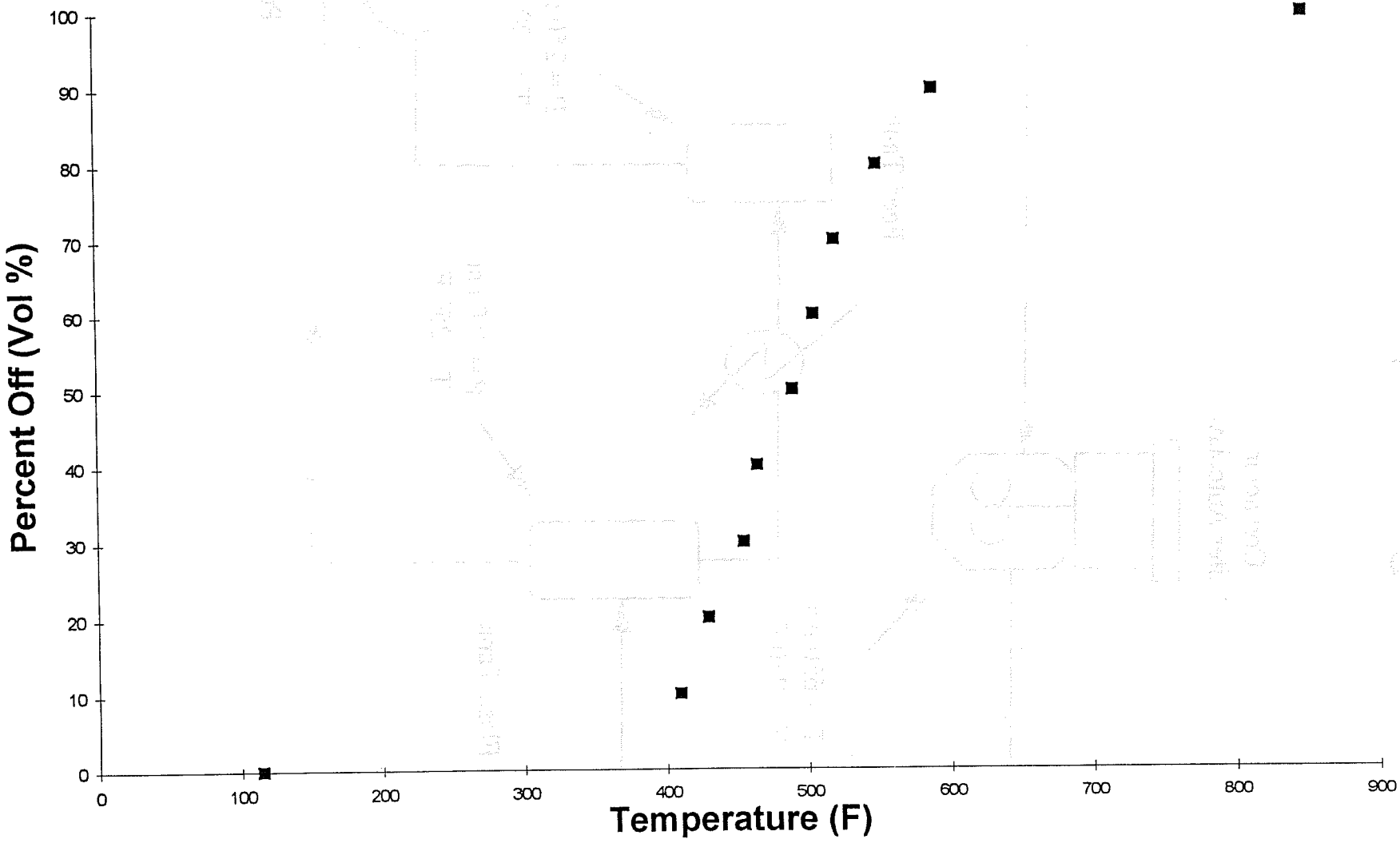


Figure 4 Experimental Unit

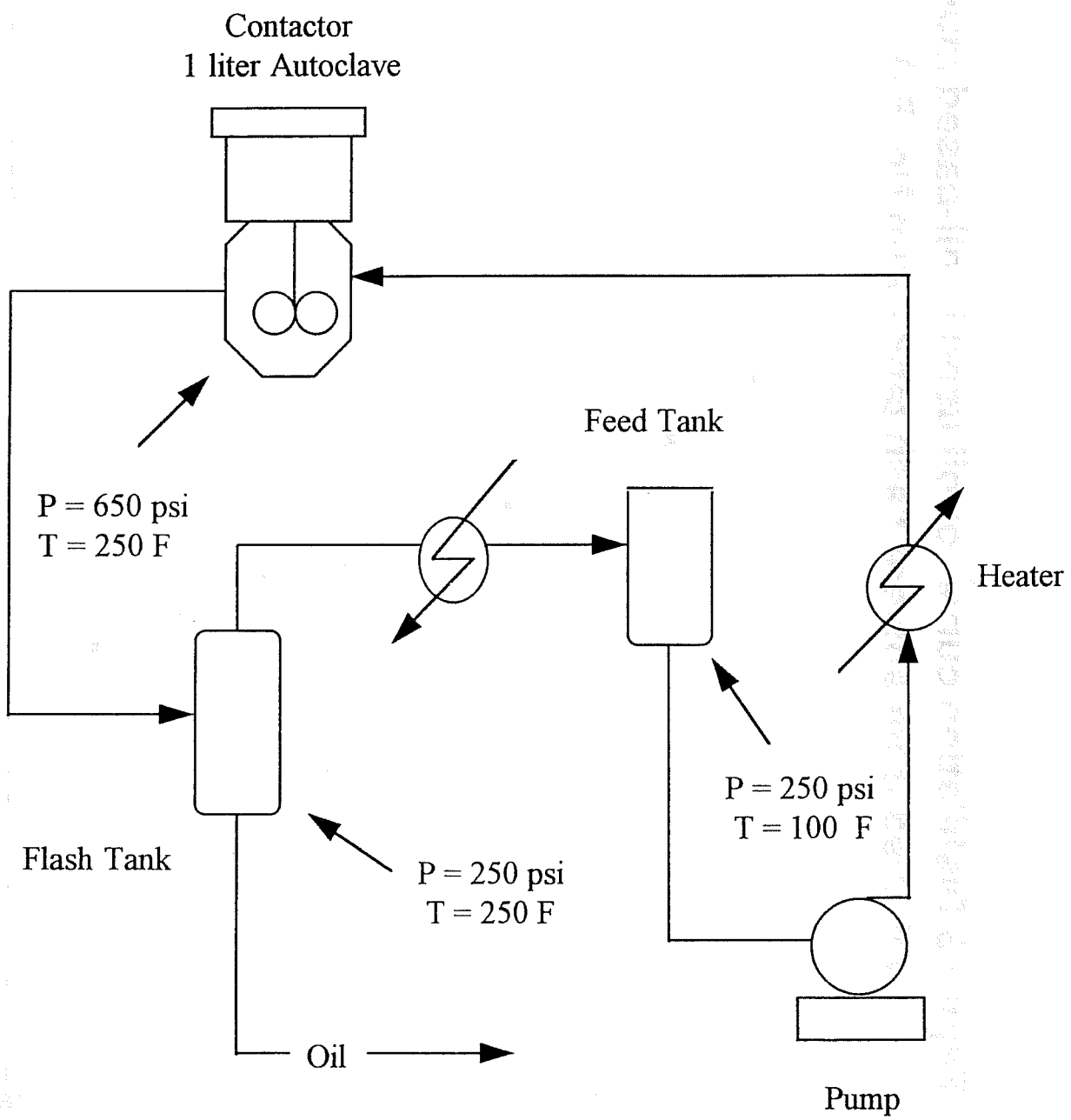


Figure 5 Pyrolysis GC results HFC 134a Run No. F1

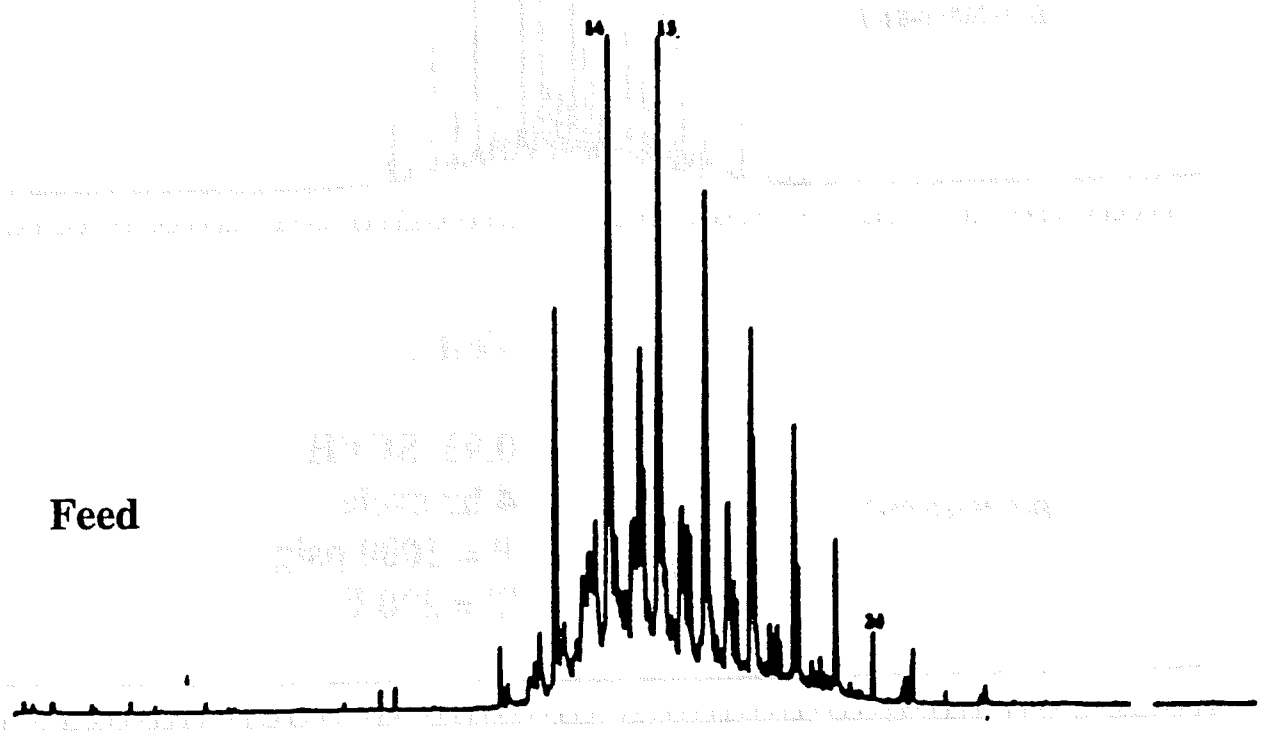
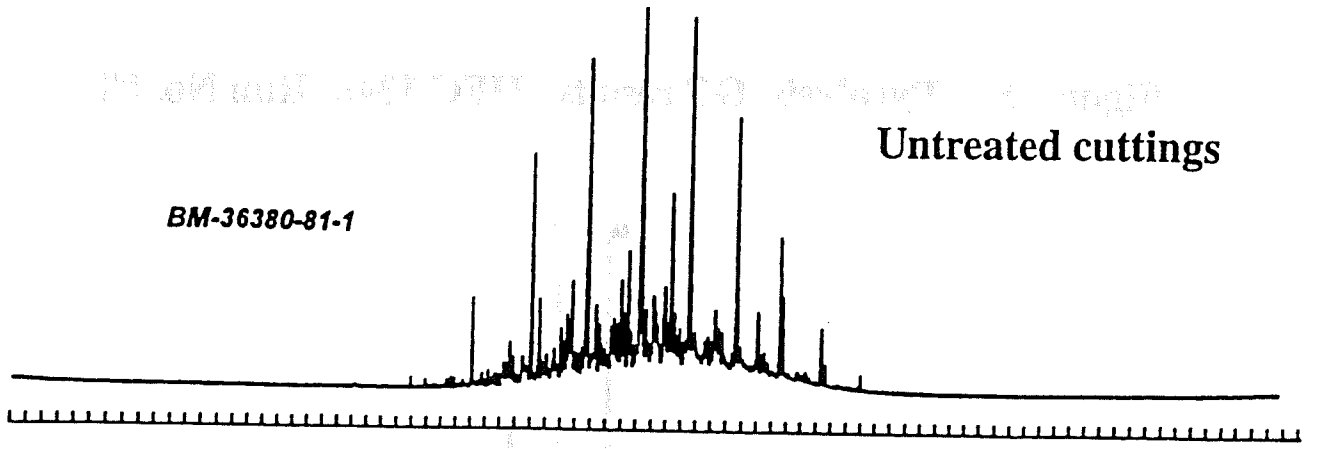
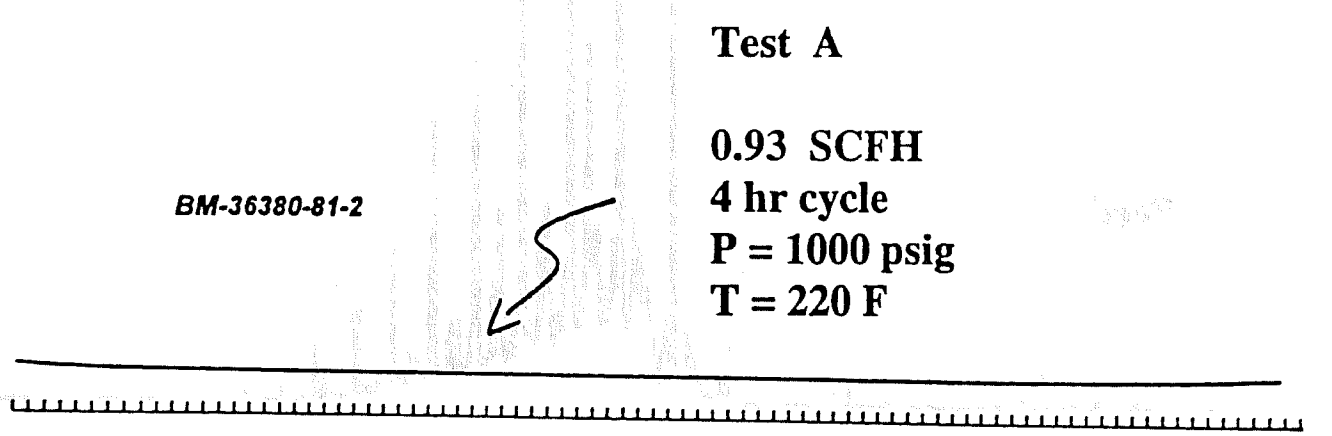
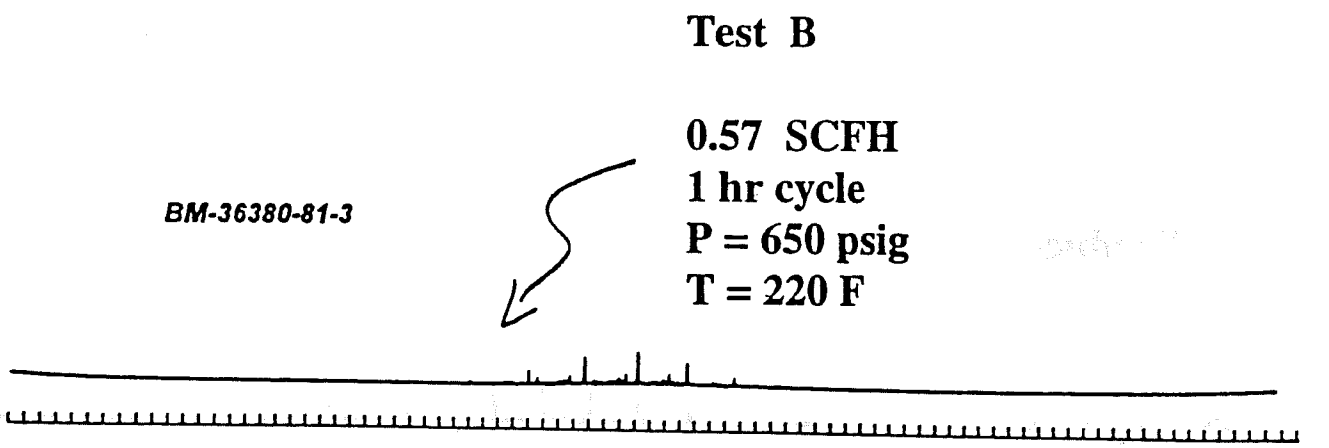


Figure 6 Pyrolysis GC results - Propane







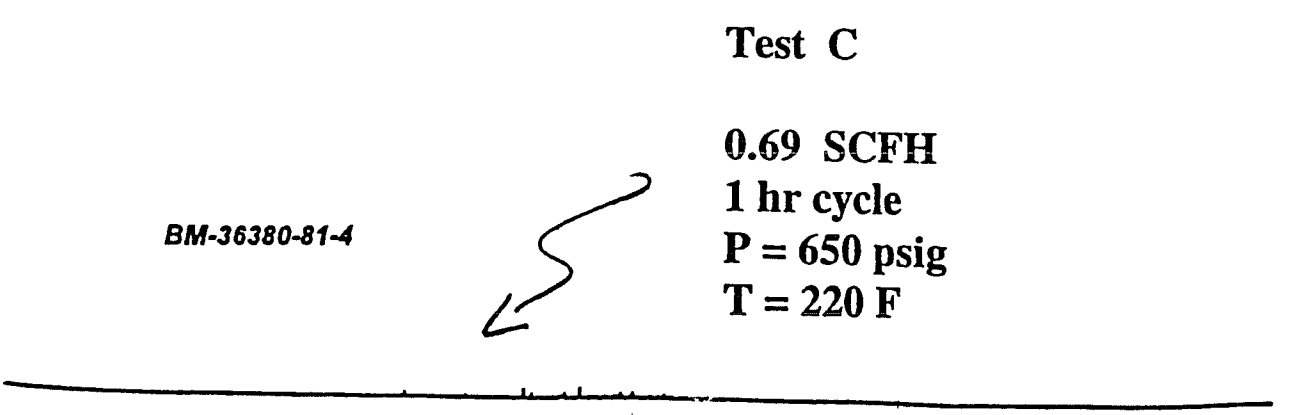


Figure 7 - Freon 134a Extraction Results

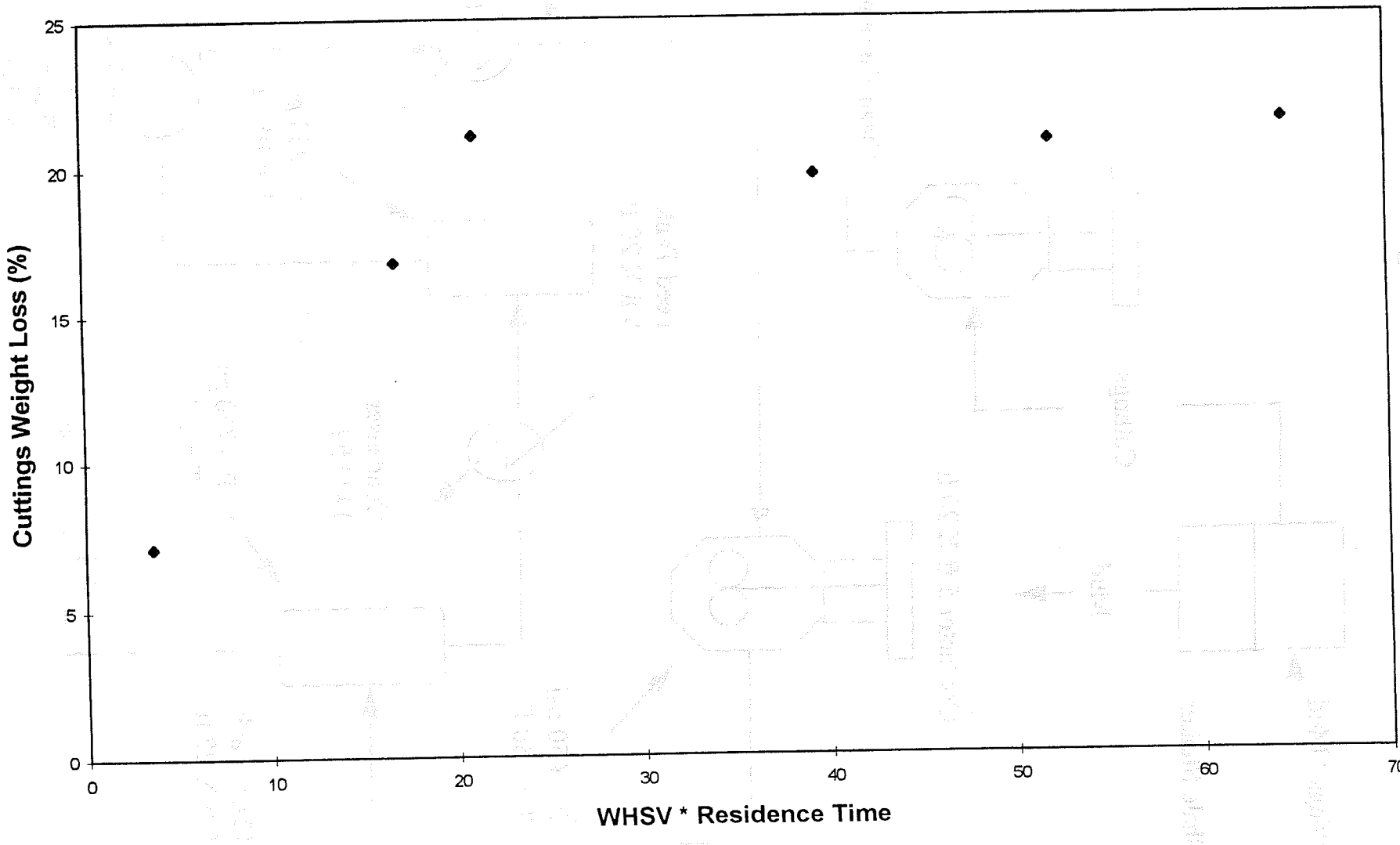


Figure 8 Commercial Cuttings Clean-up Process

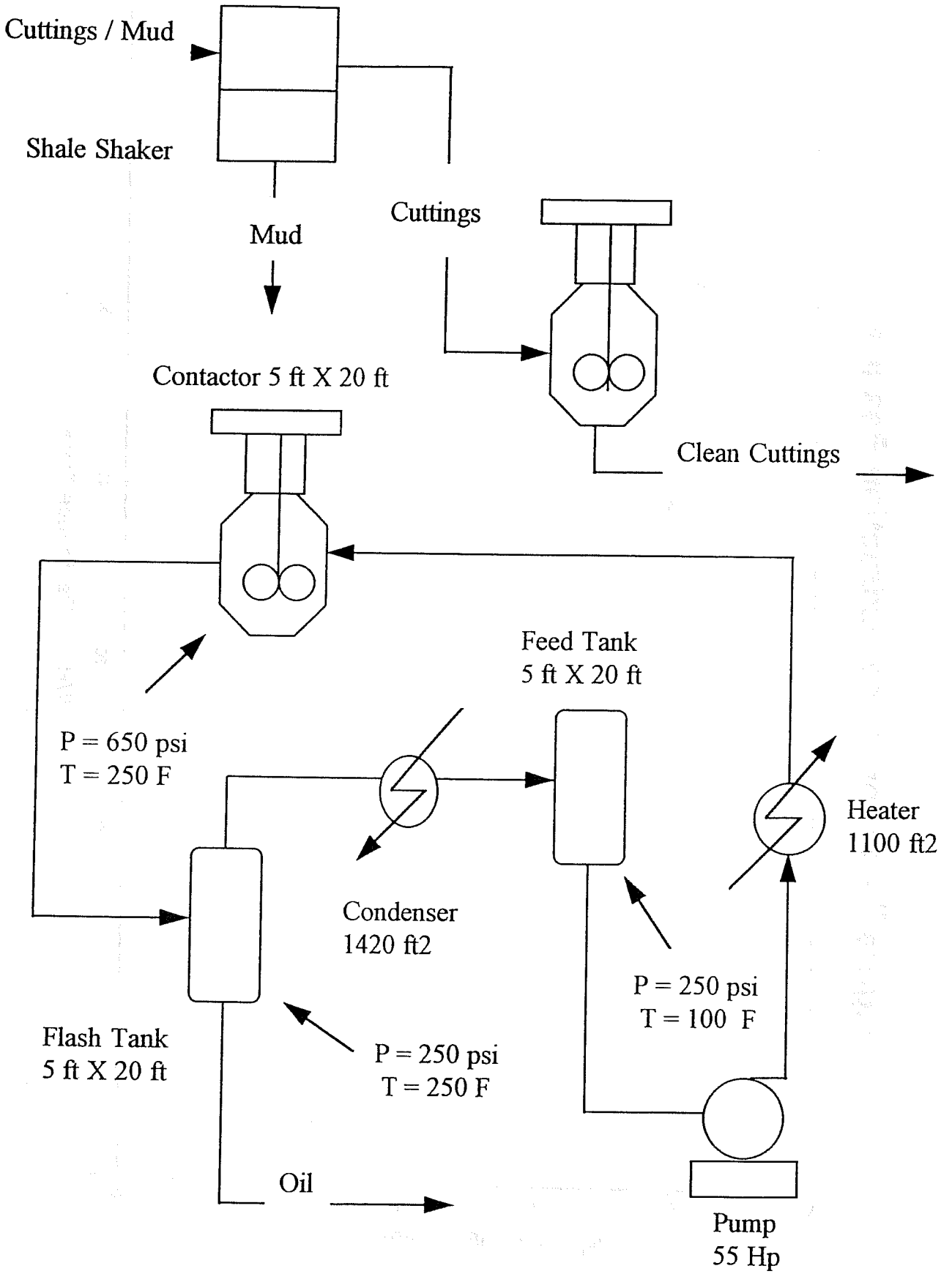
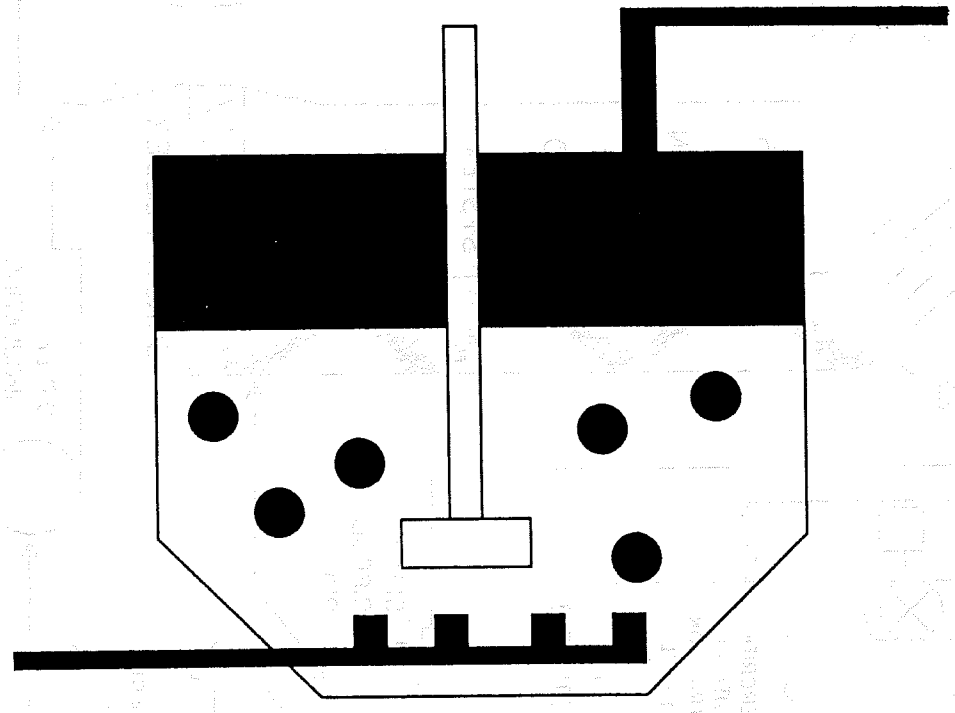


Figure 9 Modeling Considerations



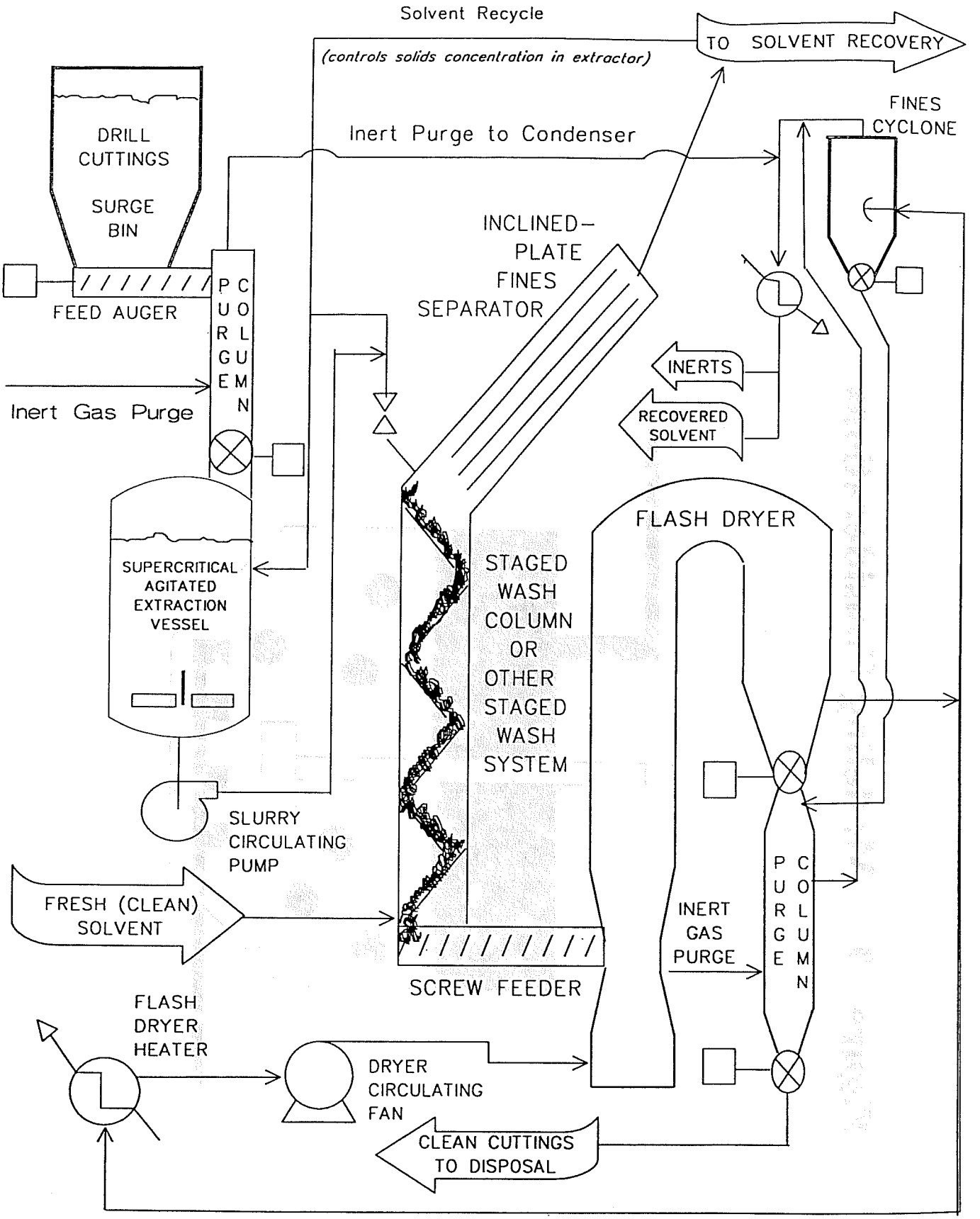


Figure 10. Illustrative Process Flow Scheme of an Extraction System for Oil-Contaminated Drill Cuttings Clean-up

Table 1

Properties of rock cuttings used in HFC 134a experiments.

Average particle size	6.9 μm (Std Dev. = 8.3 μm)
Surface area by multi-point BET	6.7 m^2 / g
Volume	6.7 E -4 cm^3 / g

Table 2 - Solvent Properties

Freon 134a (1,1,1,2 tetrafluoroethane)

- Molecular weight = 102.0 lb/lbmol
- Critical temperature (Tc) = 214.1 F
- Critical pressure (Pc) = 589.4 psia
- Normal boiling point = -14.8 F
- Liquid density (60 F) = 77.4 lb/ft3

Propane

- Molecular weight = 44.1 lb/lbmol
- Critical temperature (Tc) = 206.0 F
- Critical pressure (Pc) = 616.0 psia
- Normal boiling point = - 43.8 F
- Liquid density (60 F) = 31.6 lb/ft3

Table 3 Pilot plant test conditions - HFC 134A

Run No.	HFC Flow	Cuttings Charge	Residence Time	Cuttings Weight Loss	WHSV
F1	5.3 SCFH	260 g	3 hr	21.5 %	2.5 / hr
F2	3.0 SCFH	256 g	1 hr	16.8 %	1.4 / hr
F3	5.0 SCFH	279 g	2 hr	19.7 %	2.2 / hr
F4	22.6 SCFH	264 g	2.5 hr	20.8 %	10.4 / hr
F5	22.6 SCFH	251 g	1 hr	21.1 %	11.0 / hr
F6	36.0 SCFH	252 g	0.5 hr	7.1 %	17.4 / hr

NOTE: Weight Hourly Space Velocity = mass flowrate of the solvent / mass of cuttings charged to the contactor.

HFC flow is measured in standard cubic feet per hour (SCFH) at 60 F and 1 atm.

Table 4 - Commercial Unit Design Premises

- Cuttings production rate 12,000 lb/hr (penetration rate of 300 ft/hr)
- Freon 134a solvent
- Contactor mass hourly space velocity - 10 / hr
- Contactor pressure - 650 psia (Pr = 1.10)
- Contactor temperature - 250 F (Tr = 1.05)
- Contactor residence time - 2 hr
- Solvent flash pressure - 250 psia (Pr = 0.42)
- Heat exchange - sea water

Table 5 - Cost Estimate Results

(US Gulf Coast - 2nd quarter 1995)

Capital cost - $ 4.8 mm (offshore basis)

Operating cost - $ 120,000 / yr

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