Bioremediation of Hydrocarbon-contaminated Soil

Aerobic Biodegradation

of Petroleum Hydrocarbons

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Abstract

One of the most widespread environmental challenges in the United States today is remediation of petroleum hydrocarbons contaminating groundwater, soils, oily sludges, and wastewaters. Bioremediation is a promising and popular alternative, but its successful application requires that three characteristics of petroleum biodegradation be fully understood and incorporated into the design and operation of a bioremediation system. First, unique aspects of the biochemistry of petroleum biodegradation creates exceptional needs for oxygen supply. Second, the large majority of the hydrocarbons is in a nonaqueous phase and must be made available for microbial transformation by phase transfers. Third, documentation that the hydrocarbons actually have been degraded is difficult to obtain. Special attention must be given to monitoring strategies that provide evidence capable of proving or disproving that biodegradation has been realized.

INTRODUCTION

Contamination by petroleum hydrocarbons is a widespread phenomenon. Some types of contamination, such as tanker spills on open waterways and leaking storage tanks that contaminate groundwater used for drinking water, garner headlines and intense publicity for the petroleum industry. Other examples are less sensational, but more widespread: for example, wastewaters from refineries and ship bilges and oily sludges from refineries.

Whether the contamination is sensational or mundane, the petroleum industry is seeking reliable and cost-effective means for treatment and remediation. Among the most promising alternatives is bioremediation, whose promise comes in part from its ability to convert the contaminating hydrocarbons into innocuous products: H_2O, CO_2 and biomass. In addition, bioremediation requires neither expensive reagents nor extreme reaction conditions, factors driving up the costs of some cleanup alternatives

Petroleum contamination usually involves hundreds to thousands of organic compounds, because petroleum-based materials, from crude oil through refined derivatives, are complex mixtures of normal and branched alkanes, alkenes, cycloalkanes, and aromatics [1-4]. For example, straight-run gasolines have roughly equal contents of n-alkanes, branched alkanes, cycloalkanes, and aromatics with 5 to 10 carbons [1,3,4]. Catalytically cracked gasolines are more enriched in alkenes and aromatics, but significantly depleted in alkanes. Kerosene and jet fuel have substantially longer carbon chains than do gasolines (12 to 18 versus 5 to 10), while oils and waxes are even longer [1,3].

Although the contamination mixtures are complex, they usually exhibit three properties that are important to bioremediation:

- The carbon is highly reduced.
- The water solubility is very low for the larger molecules and also for the smaller molecules when a nonaqueous phase of the larger molecules is present.
- The hydrocarbon molecules often are comprised only of C and H.

These three properties lead directly to four factors that control the success of a bioremediation scheme:

- The highly reduced state and unique biochemistry of the hydrocarbons create exceptional needs for oxygen.
- The low solubility of the hydrocarbons makes their availability for biodegradation a rate-limiting factor in bioremediation.
- Documenting petroleum biodegradation is made more difficult by its partitioning to the nonaqueous phase and its lack of "telltale" products.
- The hydrocarbons' highly reduced state, the need for aerobic biodegradation, and lack of inorganic constituents within the hydrocarbon molecules can create a significant demand for inorganic nutrients, particularly N and P.

This paper discusses the first three factors. The fourth factor, nutrient requirements, is less unique and is discussed in many basic texts on microbiology, as well as in publications directed specifically toward the microbiology of bioremediation [1,5-7]. The objectives here are to identify the most fundamental factors and to link them directly to the practice of hydrocarbon bioremediation. For more detailed information, the reader can find critical reviews and extensive citations in Rittmann et al. [1], NRC [5], and references provided in them.

THE BIOCHEMISTRY OF PETROLEUM BIODEGRADATION

Bioremediation of petroleum hydrocarbons is almost always an aerobic process, which means that dissolved oxygen must be supplied as a cosubstrate. A very important consideration is that oxygen is utilized in two distinctly different ways by hydrocarbon-degrading bacteria: initial activation and respiration.

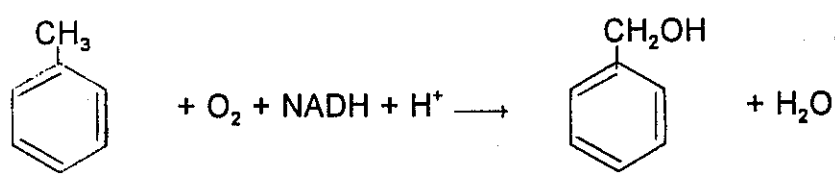
Because the hydrocarbons are comprised solely of C and H, they need to be "activated" before they can enter the metabolic pathways common to most aerobic heterotrophs. Activation in this case means insertion of oxygen (O) into the molecule. This insertion creates alcohols, which are accessible to common degradative enzymes and are more water soluble.

The activation reactions are oxygenations, which require dissolved O_2 and an intracellular source of electrons as cosubstrates. A good example is the monooxygenation of decane

$$CH_3(CH_2)_8CH_3 + O_2 + NADH + H^+ \longrightarrow$$
$$CH_3(CH_2)_8CH_2OH + NAD^+ + H_2O$$

Here, one molecule of O_2 is inserted into the terminal methyl group to create the alcohol decanol. The C in the terminal group is oxidized by the two electrons, reducing that O from oxidation state zero to minus 2. The second O in O_2 is reduced by two electrons from NADH (an intracellular electron carrier), producing H_2O and the oxidized carrier (NAD^+).

A second example of monooxygenation occurs with toluene.



The patterns of inserting one O to form an alcohol and using NADH to form H_2O hold here, as well.

Another variation on activation is dioxygenation, the insertion of both Os from O_2. A good example is benzene

The overall reaction produces catechol, a diol or double alcohol.

These activations by oxygenation make the molecules susceptible to subsequent oxidation reactions that use oxygen in the second way. Another very key feature of oxygenations is that, although the hydrocarbon molecule is oxidized, no reduced electron carriers (like NADH) are produced; in fact, the monooxygenations consume NADH.

Once a hydrocarbon molecule is activated, it can be catabolized by the routine oxidation reactions that do not involve O_2 as a direct substrate. These reactions are sequential dehydrogenations and hydroxylations that lead from alcohols to carboxylic acids. An example is for decanol.

$$CH_3(CH_2)_8CH_2OH + NAD^+ \longrightarrow CH_3(CH_2)_8CHO + NADH + H^+$$
$$CH_3(CH_2)_8CHO + NAD^+ + H_2O \longrightarrow CH_3(CH_2)_8COOH + NADH + H^+$$

The first step is a dehydrogenation, which transfers 2 electrons from the alcohol to form NADH and the aldehyde. Subsequently, the aldehyde is oxidized by 2 electrons to form the carboxylic acid; NADH is produced, while the inserted O comes from H_2O.

Once aliphatic carboxylic acids are formed, they undergo β-oxidation, which involves stepwise 2-electron oxidations that yield acetic acid (CH_3COOH) groups. The net reaction for one round of β-oxidation of decanoic acid is

$$CH_3(CH_2)_8COOH + FAD + NAD^+ + 2\ H_2O \longrightarrow$$
$$CH_3(CH_2)_6COOH + CH_3COOH + FADH_2 + NADH + H^+$$

where FAD and FADH are oxidized and reduced forms of another intracellular electron carrier.

The produced acetic acid can enter the tricarboxylic-acid (TCA) cycle, which also is a series of 2-electron oxidations that eventually lead to full oxidation of both carbons to CO_2. The net effect of the TCA cycle is

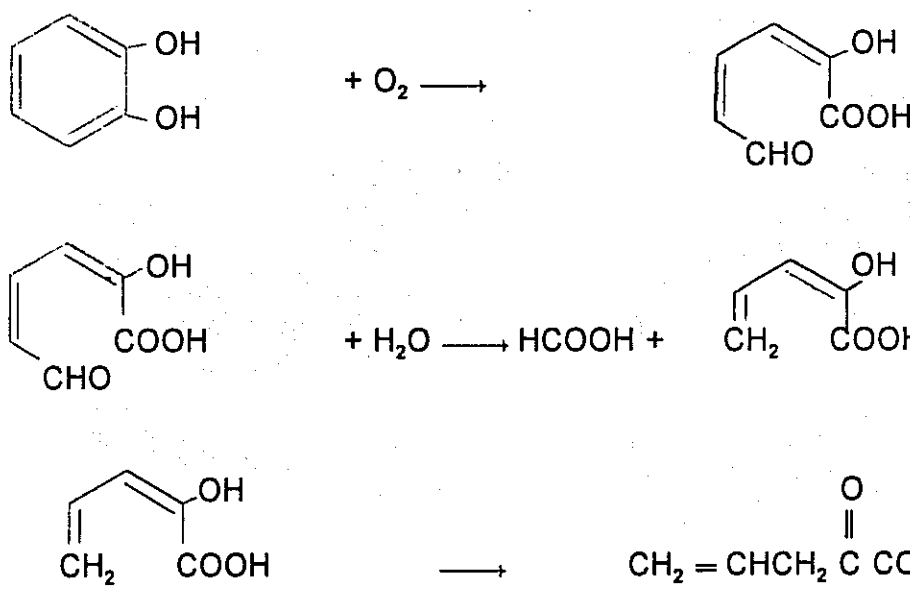
$$CH_3COOH + 2\ H_2O + 2\ NAD^+ + NADP^+ + FAD^+ \longrightarrow$$
$$2\ CO_2 + 2\ NADH + NADPH + FADH_2 + 4\ H^+$$

$NADP^+$ and NADPH are intracellular electron carriers closely related to NAD and NADH.

The sum of all reactions shown here for decanol produces octanoic acid ($CH_3(CH_2)_6COOH$), 2 CO_2, 5 NADH, 2 $FADH_2$, and 1 NADPH. The last three terms are reduced electron carriers containing (5 + 2 + 1) x 2 = 16 electron equivalents. These electron equivalents are transferred to O_2 through respiration. Thus, oxygen is the terminal electron acceptor needed to regenerate the oxidized forms of the electron carriers. Respiration also generates the intracellular energy carrier ATP by creating a cross-membrane proton-motive force as part of the electron-transfer scheme from the reduced carriers to the terminal electron acceptor.

Aromatic hydrocarbons undergo somewhat different pathways, some of which require further oxygenations that allow ring cleavage. Once the ring is cleaved, reactions similar to those in β-oxidation generate acetic acid, which then enters the TCA cycle and is oxidized to form reduced electron carriers.

An example of further aromatic activation is the meta pathway for catechol, the first three steps of which are shown here.



The last product—2-oxopent-4-eneoate—undergoes a hydrolysis step that leads to acetaldehyde and pyruvate, both of which are precursors to the TCA cycle.

Because hydrocarbons have very reduced carbon, complete oxidation to CO_2 and H_2O (called mineralization) has a high total demand for oxygen. For example, mineralization of decane requires 4.13 g O_2/g C, while mineralization of benzene requires 3.33 g O_2/g C. These high demands, coupled with the low solubility of dissolved oxygen (about 10 mg/ℓ at 15°C), explain why bioremediation technologies used for petroleum hydrocarbons emphasize oxygen supply [1,5,8].

Although the total oxygen demand is higher for aliphatics, the activation portion is much larger for aromatics. For decane, only 0.24 g O_2/g C is needed for the oxygenations, leaving 3.89 g O_2/g C for respiration and energy generation. On the other hand, benzene uses 0.88 g O_2/g C for initial oxygenations, leaving 2.45 g O_2/g C for respiration. Since O_2 is a direct and obligate cosubstrate in the activation reactions, the O_2 demand to activate aromatics is relatively and absolutely more important than it is for aliphatics. This suggests that oxygen limitation may be more serious for aromatics biodegradation, even though aliphatics consume more oxygen per gram of C. This limitation may be further exacerbated by recent evidence suggesting that oxygenation enzymes may be more sensitive to oxygen limitations than are the respiratory enzymes [9].

Because aromatics consume substantially more O_2 in oxygenation reactions, they have far fewer electrons to transfer from reduced electron carriers to the terminal electron acceptor. This should mean that cell yields (g dry weight/g hydrocarbon C) ought to be substantially lower for cells growing on aromatics.

While O_2 is an obligate cosubstrate for the oxygenation reactions, it is not the only compound able to serve as the terminal electron acceptor for respiration. Nitrate (NO_3^-) is an excellent substitute that can be utilized by a wide range of aerobic heterotrophs when dissolved-oxygen concentrations are low. At least in principle, SO_4^{2-}, Fe^{3+}, and CO_2 could be used as well. Thus, it seems feasible that relatively small concentrations of O_2 could be used for the initial oxygenation reactions, while alternative electron acceptors fulfill the respiration needs. This scenario seems more viable for the aliphatic hydrocarbons than for the aromatics. The cells should experience reduced yields and specific growth rates when alternative electron acceptors are used.

AVAILABILITY OF PETROLEUM SUBSTRATES

The physiology of bacteria requires that they live in the aqueous phase. Even though some petroleum-degrading bacteria are known to adhere to the hydrocarbon surface [1], the microorganisms are in the water phase. Therefore, the aqueous concentration of a hydrocarbon is a key determinant of its rate of biodegradation. Very low concentrations mean low degradation rates and work against successful bioremediation.

The smaller hydrocarbons have relatively high water solubilities (C_p). Example C_p values come from some of the common compounds in gasoline [1]: n-pentane, 62 mg/ℓ; 2-methylbutane, 48 mg/ℓ; cyclohexane, 55 mg/ℓ; benzene, 1780 mg/ℓ; and toluene, 515 mg/ℓ. Nevertheless, being in mixtures with larger, less soluble components makes the actual water-saturation concentration (C_s) much less than the water solubility in contact with the next compound. The relationship is

$$C_s = C_p X$$

where X is the mole fraction of the component in the oily phase. This mole-fraction effect means that the small molecules, as well as the large molecules, can have low C_s values that can limit their biodegradation rates.

The most general pathway by which a hydrocarbon enters the aqueous phase is dissolution. The rate of dissolution, which puts an upper limit on the rate of biodegradation, is given by

$$J = k_m (C_s - C)$$

where J is the dissolution flux (mg/m^2-day), k_m is a mass transport coefficient (ℓ/m^2-day) that depends on hydrodynamic conditions, and C is the actual aqueous-phase concentration (mg/ℓ). For a unit volume of water, the rate of dissolution, r_{diss} (mg/m^3-day), depends on J and the area of the hydrocarbon/water interface, a (m^{-1}), by

$$r_{diss} = Ja$$

The rate of dissolution becomes small when k_m, a, or C_s-C is small. Clearly, a low C_s limits the rates of dissolution and biodegradation.

Biodegradation and dissolution interact, because biodegradation serves as a sink for dissolved hydrocarbon and lowers C. Thus, biodegradation enhances dissolution, which provides a greater supply of hydrocarbon for biodegradation. Work in the author's laboratory by Seagren [10-12] has quantified the enhancement effect from biodegradation by bacteria attached to porous media in contact with pool or ganglia of

hydrocarbon. The enhancement effect can be dramatic, perhaps tenfold or more for high microbial activities, as long as the advection sink is not already large. A tenfold increase in dissolution rate should translate into a tenfold reduction in the cleanup time.

For very low-solubility components, direct contact of the bacteria and the hydrocarbon surface frequently is required. Adhesion may simply be a means to reduce mass-transport distances for dissolved solute, or a more direct uptake mechanism may be involved. In either case, the microorganisms use adhesion to increase the rate of transfer of hydrocarbon molecules from the nonaqueous phase to themselves.

In some cases, bacteria produce surface-active agents that reduce the surface tension and facilitate emulsification. Commercial dispersants also can be used for the same purpose. Growth of hydrocarbon-degrading bacteria in well mixed systems, such as slurry reactors, can be greatly accelerated through emulsification by applying surface-active agents and vigorous agitation. The mechanism for the acceleration is an increase in the specific surface area, *a*, through creation of micelle-sized hydrocarbon droplets, a process sometimes called pseudosolubilization. Thus, r_{diss} increases through an increase in *a* when emulsification is possible. Emulsification is possible in slurry reactors and liquid streams. Its role in open waters is not fully understood.

For in situ bioremediation and land farming, emulsification is highly improbable, as the soils cannot be agitated vigorously. For example, Rittmann and Johnson [13] found that a dispersant that significantly accelerated biodegradation of lubricating oil on liquid and slurry reactors had no effect in static soil plots. On the other hand, large doses of surfactants sometimes are used to create micelles of the surfactant itself. These surfactant micelles can extract components from the petroleum phase. If the micelles are mobile, a flushing scheme can be used to accelerate hydrocarbon removal through mobilization within the micelles.

Mobilization of petroleum hydrocarbons by use of surfactant micelles brings about a very different result than does emulsification of the petroleum hydrocarbons by small doses of surfactants. In general, mobilization decreases the aqueous-phase concentration of the petroleum components; this decrease generally slows biodegradation rates. Thus, emulsification usually speeds biodegradation, while mobilization usually slows it. This distinction has been confused in the past by the unfortunate use of the term "solubilization" for what is more properly called mobilization.

DOCUMENTING BIOREMEDIATION

In many cases, documenting that biodegradation has occurred and brought about a cleanup is a difficult and controversial task. Five factors make the task especially challenging.

- Most of the contamination is not truly dissolved in the water, which is easiest to sample and often is the focus of regulation. This problem is most severe for contaminated soils, where hydrocarbons are trapped as a nonaqueous-phase liquid (NAPL) or adsorbed to the soil surfaces.

- The contamination is nonhomogeneous. Samples taken from different locations give different results, thereby creating uncertainty. The problem of nonhomogeneity is very serious for *in situ* bioremediation, but can be partially overcome by mechanical mixing in *ex situ* treatment.

- The regulations often focus on the most water-soluble components, but their fate is controlled by the larger, more hydrophobic components, which can serve as a long-term source of the more soluble components and whose biodegradation usually is slow. This multi-component problem is important in all settings, although it may be most severe for oily sludges.

- In most bioremediation applications, abiotic mechanisms also can be responsible for decreases in aqueous-phase concentrations: e.g., advection in a flowing water stream, volatilization to a gas phase, and adsorption to solids.

- The obvious products of hydrocarbon biodegradation can be confounded. For example, the generation of CO_2 leads to an increase in inorganic carbon in the water, but dissolution of minerals (e.g., from $CaCO_3$) also adds to the pool of inorganic carbon. While the consumption of oxygen is strongly tied to hydrocarbon biodegradation, oxidation of Fe^{2+} or mixing with deoxygenated water also causes decreases in dissolved oxygen. Finally, the large increases in hydrocarbon-degrading bacteria can be missed, because the bacteria are attached to solids and highly localized.

Recently, the National Research Council's Committee on *In Situ* Bioremediation studied the dilemma of documentation. The multidisciplinary panel published its findings in *In Situ Bioremediation: When Does It Work?* [5], which provides its readers with a fundamental understanding of bioremediation and guidelines for designing protocols that effectively evaluate a bioremediation scheme in the field. While specifically addressing the confounding factors inherent to in situ bioremediation, the NRC book is directly pertinent to *ex situ* bioremediation technology and bioremediation in open waters.

The NRC committee concludes that bioremediation is proven a success only when microbial activity at the site is linked to the observed loss of contaminants. An evaluation strategy requires three types of evidence:

1. Documented loss of contaminants from the materials being bioremediated.

2. Laboratory assays or strong evidence from the peer-reviewed literature that microorganisms in site samples have the *potential* to transform the contaminants under the expected bioremediation conditions.

3. One or more pieces of evidence showing that the biodegradation potential is *actually realized* during the bioremediation.

The third type of evidence is the most difficult to obtain, but it is the necessary link between the loss of contaminants and the potential for biodegradation. In most cases, the complexities of the contaminated materials make it necessary to use a range of different measurements. Thus, convergent lines of independent evidence should be put together to build a logical, consistent case for or against success.

The NRC report [5], as well as derivative summaries [14,15], summarized techniques that can be used to obtain the third type of evidence. The reader should consult these sources for the full suite of options. Several of the techniques most important for petroleum hydrocarbons are reviewed here.

Probably the most dramatic evidence of biodegradation of petroleum hydrocarbons is consumption of oxygen. Particular care must be taken to ensure that concentrations are representative of the water (or gas) and not altered by atmospheric contamination. Direct probe measurements usually are the most satisfactory.

Because the oxidation of certain inorganics also can consume oxygen, concentrations of Fe^{3+}, Fe^{2+}, Mn^{4+}, Mn^{2+}, NH_4^+, NO_2^-, and NO_3^- should be measured in coordination with the oxygen measurements if these inorganic ions are present. A further check can be obtained by coincident measurements of the alkalinity, since oxidation of inorganic ions often consumes alkalinity.

The second most important piece of evidence is the increase in total inorganic carbon (TIC). The oxidation of hydrocarbons directly produces CO_2, but all or part of that CO_2 is absorbed by water, forming mostly HCO_3^- and H_2CO_3. Thus, the TIC of the water and a gas phase should increase in proportion to the mineralization of the C in the hydrocarbon. However,

absorption of CO_2 does not alter the water's alkalinity. Therefore, oxygen consumption accompanied by an increase in TIC and no change in alkalinity is strong evidence of hydrocarbon biodegradation.

Concentrations of alternative electron acceptors—most particularly NO_3^-, NO_2^-, SO_4^{2-}, and Fe^{3+}—should be measured in the water, if they are present. Although O_2 is critical for the initial activation steps of hydrocarbon biodegradation, the respiratory oxidations could occur with consumption of an alternate electron acceptor.

When changes in TIC concentration possibly are confounded by dissolution of carbonate minerals, the TIC in liquid and gas samples can be analyzed for the ratio of stable carbon isotopes, ^{13}C:^{12}C. Inorganic carbon derived from mineral deposits is substantially more enriched in ^{13}C than is inorganic carbon produced through oxidation of petroleum. Thus, if the TIC obtained from samples has a ^{13}C:^{12}C ratio lower than the ratio for carbon derived from carbonate minerals, it is evidence of bioremediation.

Increases in microbial activity or numbers can be strong evidence for successful bioremediation. On the other hand, not finding large increases need not be interpreted as evidence of failure, because of the severe problems obtaining representative samples of what is usually highly localized microbial activity. The most relevant samples are taken from the solid phase (when one exists), since most bacteria are attached in soil and slurry systems.

Existing enumeration techniques are notoriously unreliable for quantification. Better quantification and more information-rich data will be obtained when more sophisticated tools, including those from molecular biology, are applied. Examples include oligonucleotide probes specific for key degradative genes or for a class of microorganisms, polymerase-chain-reaction (PCR) amplification of the DNA for selected microorganisms, and activity assays specific for key degradation reactions.

SUMMARY

Although biodegradation of petroleum hydrocarbons is well established, its implementation in practice is far from trivial. In particular, special attention must be given to:

- the large consumption and dual role of oxygen as an electron acceptor
- the low solubility, which limits the availability of hydrocarbons for biodegradation

- the practical difficulties documenting successful bioremediation in a field setting

Despite these challenges, bioremediation of petroleum hydrocarbons is happening on a major scale and likely will increase in the future. Its ultimate contribution to solving the problems of petroleum contamination will depend on the attention we give to these scientific and technical issues.

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Hydrocarbon and Produced Water Contaminated Soil and Pit Waste Remediation

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ABSTRACT

Exploration and Production [E&P] operations worldwide, generate more soils and pit wastes contaminated with hydrocarbons, metals and chlorides than any other wastes, except produced waters. Transporting contaminated wastes offsite result in operators losing control of the wastes. Additionally, off-site disposal of wastes offsite consumes landfill capacity. Field experience during the past 8-10 years demonstrates contaminated soils and pit wastes can be bioremediated onsite at low cost while retaining control of the waste. Moreover, bioremediation results in reducing hydrocarbon content to acceptable safe levels. Also, soil amendments convert sodic soils to calcium base soils, encouraging leaching of the chlorides and revegetation. The authors illustrate land treatment and bioremediation technologies by providing a scenario detailing necessary data, calculations and limiting constituents required for successful remediation of crude oil and produced water contaminated soil. The methods illustrated in the paper apply equally to pit wastes and soils throughout the world.

BACKGROUND

The public and regulators have expressed concern regarding the environmental impact of Exploration and Production waste on the environment [EPA, 1987]. American Petroleum Institute [API], anticipating this concern, commissioned a study of the effect of drilling fluid components on plants and soils [Miller and Honarvar, 1975]. Deuel [1991], Moseley [1984] and Miller and Honarvar [1975] showed soluble chloride and exchangeable sodium are the major ions migrating in soil

causing harmful effects on the soil and plant growth. These ions increase osmotic potential interfering with plant uptake of required nutrients and water [Murphy and Kehew (1984) and Miller, et al (1980).

Metals found in E&P wastes include chromium, cadmium and zinc [EPA, 1987]. Availability of these metals to migrate depend on pH, oxidation-reduction potential and total metal concentration; pH is the primary controlling factor. Freeman and Deuel [1984] show the solubility of metals is inversely related to pH, except barium whose solubility is directly related to pH. Typically, migration of ions in soil is limited by attenuation in clay materials.

Freeman and Deuel [1984] show controlling pH, incorporation of drilling clays in soil and improving soil structure by amendments, i.e., gypsum, humus and fertilizer, provide a viable method for remediating soils contaminated by hydrocarbons and metals. Many of these concepts are included in the Louisiana Pit Closure Rule [Rule 29-B (1990)].

PROBLEM DEFINED

The existing technical literature, with minor exceptions, recite bioremediation case studies and results, but lack design criteria which the uninitiated can follow. This lack of technical guidance leads to remediation failures and skepticism on the part of regulators.

This paper demonstrates, by sample calculations, methods for determining the required quantities of dilution, nutrients and soil amendments.

LIMITING CONSTITUENT CRITERIA

The vast majority of E&P wastes and contaminated soils are <u>not hazardous</u>. [EPA, 1987]. Accordingly, mixing or burying these wastes is environmentally acceptable and encouraged by states [Rule 29B, 1990, Statewide Rule 91, 1993].

<u>State Regulations</u>

Most states either: (1) exempt reserve pits and non-hazardous substance spills to soils from control or; (2) provide demonstration options to E&P operators. Standard operating procedures for pit closure in most states include dewatering, compacting and backfilling. Contaminated soil remediation is beginning to be regulated [Statewide Rule 91, 1993].

Within the U.S., Louisiana imposes the most severe controls on pit closure [Rule 29-B, 1990]. This rule is necessarily restrictive because of the hydrologic sensitivity of Louisiana. Rule 29-B is not applicable to all areas due to different climatic and geological conditions.

Recommended Limiting Criteria

Based on our studies, we recommend Limiting Criteria, **Table 1**, for land treatment in various wetland and upland situations. These criteria provide ample environmental protection for wetlands and uplands. Deuel and Holliday [1993] recommend additional limiting criteria for vertical dilution, dilution burial and road spreading.

Land Treatment

Land treatment renders wastes harmless through soil incorporation via dilution, chemical alteration and biodegradation. The technique provides treatment and final disposal of salts, petroleum hydrocarbons and metals. EPA [1980] demonstrated the viability of the technique as an acceptable method for disposal of municipal sewage sludge and industrial waste.

In the authors opinion, proper disposal of E&P waste/soils requires:

- Representative samples of:
  - contaminated area, or pit wastes and
  - background area
- Accurate analytical characterization of the samples
- Determination of required waste/soil amendments
- Mixing of waste/soil and amendments
- Representative samples of the closed waste/soil area
- Demonstration by analysis the limiting criteria are attained

Sampling and analysis are discussed by Deuel and Holliday [1993].

AMENDMENTS

The choice of amendments depends on the contaminants present.

pH Amendments

Waste Liquids

Aluminum sulfate, ($Al_2(SO_4)_3$) controls excess alkalinity i.e., pH >8.3, while excess acidity [low pH] is managed using lime (CaO). These amendments should be distributed onto the liquid without mechanical agitation.

Waste Solids

pH adjustments to waste solids are made by spreading the amendment on the soil/waste surface and physically mixing, i.e., disk or backhoe. Agriculture limestone ($CaCO_3$) adjusts excess acidity [low pH] and elemental sulfur (S) adjusts excess alkalinity.

Salinity Amendments

Only fresh water and a rinse or leach process reduces salts in soils and wastes. Poor soil physical structure and inherent low hydraulic conductivity prevent free exchange of salt without structural amendments, wetting agents and/or mechanical processes.

Structuring amendments aid the soil/waste by aggregation. Polyvinyl alcohols, polyacrylamides and natural plant polymers increase aggregation when mixed with soil/waste. Mechanical processes physically loosen the soil/waste allowing greater surface contact with water and amendments. Disking loosens soil/waste to a depth 6-10 inches Chiseling becomes necessary at salt contaminated sites and loosens soils to 12-18 inches.

Sodicity Amendments

Produced water or salt muds cause soil to become saline, sodic or both. Sodic soils are defined as soils having exchangeable sodium percentage [ESP] of ≧15%. Saline soils are defined as soils having a saturated paste extract electrical conductivity [EC] of >4 mmhos/cm.

Calcium amendments counteract sodicity and high salinity. If the soil/waste is both saline and sodic, calcium should be added prior to leaching. Agriculture grade gypsum ($CaSO_4$) is an effective source of calcium, but time is needed for the salt exchange to occur because of the limited solubility of gypsum.

If time is limited, soluble calcium sources, such as calcium chloride ($CaCl_2$) or calcium nitrate ($CaNO_3$), can be very effective in lowering the sodium content. These amendments work best when soil or waste solids have not yet equilibrated to a sodic condition. However, care must be exercised when using calcium nitrate since nitrate is an inorganic drinking water contaminant limited to 10 mg/l as the maximum safe concentration [40 CFR §141.11].

Organic Matter Amendments

Organic amendments such as peat moss, hay or low salt manures improve soil structure. Also, organic materials serve as a sink for salts by exchange mechanisms and dilute salts in soil solutions by increasing moisture holding capacity. Further, decomposition of the organic materials increase soil temperature thereby allowing or increasing biological action.

Bioremediation Amendments

Microorganisms

Native soil, typically, contain sufficient number and diversity in microflora to degrade hydrocarbons under controlled conditions. In rare cases, inoculation becomes necessary to off-set poor population dynamics.

Fertilizer

Nitrogen, in the form of fertilizer, is necessary for bioremediation of hydrocarbons. Ammonium nitrate, ammonium sulfate and urea constitute good sources of nitrogen. Splitting the fertilizer into 3 applications increases the effectiveness. Nitrogen must be disked into the soil to distribute the application and add oxygen to the soil. Apply nitrogen so the ratio of carbon-to-nitrogen [C:N] is 150:1. We recommend assuming crude oil is 78 percent carbon. Phosphorus (P) and potassium (K) are applied at 1/4 the nitrogen rate [C:P,K = 600:1]. Typical phosphorus and potassium are applied as a single application with the initial nitrogen treatment.

Moisture

Moisture required for effective plant growth is the amount of moisture present in a soil in equilibrium with an applied pressure of 1/3 bar. This moisture value is known as the Field Capacity. Optimum

biodegradation rates occur when the biomass is maintained at 50 to 80 percent of field capacity. In some cases, land treatment becomes impossible or uneconomical because of lack or cost of water. If water is not available either in the form of rain or applied moisture, bioremediation should not be attempted.

Remediation temperature impacts the efficacy of bioremediation. Mean soil temperatures at or above 22° C [72° F] allow remediation of hydrocarbon loading of up to 5 percent total petroleum hydrocarbons [TPH]. A 1 percent decrease in loading for each 7° C temperature reduction assures good remediation for crude oil 20° API and above. For crude oil below 20° API initial loading should be reduced to 3 percent at or above 22° C. Again, a 1 percent decrease in loading for each 7° C reduction appears satisfactory.

DILUTION PROCEDURE

Based on the sample calculations, **Appendix 1**

1. Scrape contaminated soil from spill area and spread evenly over 0.88 acres to a calculated depth of 0.3 inches .

2. Disk the 0.88 acres treatment area to a depth of 6 inches.

3. Apply the 131 pounds of gypsum to the area and disk.

4. Contour treatment area to original grade.

5. Apply 75 pounds ammonium nitrate and 50 pounds of 13-13-13 fertilizer to the treatment area to encourage vegetation. Again, this application is based on experience rather than calculations.

6. After 6 months sample, analyze and compare with target values,

SUMMARY AND DISCUSSION

Bioremediation successfully treats soils and wastes containing hydrocarbons. Typically, hydrocarbon releases to soil are easily remediated when fresh [recent spills]. Produced water spills are more difficult to remediate since extensive dilution, soil amendments and/or tillage is required. Additionally, lack of fresh water or cost of water may prohibit remediation. Accordingly, retiring the land from agronomic productivity may be necessitated and cost effective.

The limiting criteria recommended in the paper result from 8-10 years of hands-on field work. Achieving the recommended criteria levels is assured, if nutrients, water and oxygen are provided for hydrocarbon containing soils and wastes.

Obtaining representative samples and accurate analysis represents the most pervasive problem associated with *in situ* soil and waste remediation. Samples of affected and background areas must represent the areas. The analytical protocols must accurately characterize the level of contamination. Characterizing the contaminants represents a particular problem since few soil analytical procedures are available [Deuel and Holliday 1993]. The use of analytical methods developed for waste water guarantee improper characterization.

Once having determined the soil amendments of choice and the amounts, those amendments must be utilized properly. Phosphorus, potassium and gypsum are added to the soil/waste in one application. On the other hand, nitrogen is added, typically, in 3 applications:

The second and third applications should be separated by 6-8 weeks.

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Table 1

Limiting Criteria For Land Treatment of Soils Containing Metals and Organic Materials.

	Wetlands			Uplands	
	Brackish	Freshwater Submerged	Freshwater Elevated	Forest/ Recreational	Farming/ Residential
pH	6-9	6-9	6-9	6-8	6-8
EC (mmhos/cm)	—	—	8-50	4-8	2-4
SAR	—	—	14-100	<14	<12
CEC (meq/100g)	>15	>15	>15	>15	>15
ESP (%)	—	—	<25	<15	<15

Heavy Metals (mg/kg)	Wetlands	Uplands
Arsenic	<10	<40
Barium	<20,000	<40,000
Cadmium	<10	<10
Chromium	<500	<500
Lead	<500	<500
Mercury	<10	<10
Selenium	<10	<10
Silver	<10	<10
Zinc	<500	<500

Organics (%)	Wetlands	Uplands
Oil&Grease	<1	<2

APPENDIX 1
Sample Calculations

Spill Description

A flowline leak causes 1.6 m^3 [10 BBL] of high gravity [38° API] oil and 4.6 m^3 [40 BBL] of saline produced water to spill onto native sandy soil. Assume the spill contaminates 0.02 hectares [0.05 acres] to a depth of 6 in.

Oil Remediation Calculations

Assuming the oil floated uniformly on the produced water and affects the same spatial volume. Accordingly, the resulting oil loading is about 3.4 percent.

Also, hydrocarbon reduction results from dilution. Dilution, X required for Total Petroleum Hydrocarbon [TPH] reduction:

Soil TPH = 3.4 percent.
Target TPH = 1 TPH
Background TPH = 0.01 percent
Contaminated soil volume
= 0.05 acres * 43560 ft^2/ac x 0.5 ft
= 1089 ft^3

$$TPH = \frac{(3.4TPH)(1089\,ft^3) + Xft^3 * 0.01TPH}{1089\,ft^3 + Xft^3}$$

or X= $2640\,ft^3$

Carbon content of oil in the soil, mg/kg.

$$C,\% = TPH,\% * 0.78 = 3.4 * 0.78$$
$$= 2.65\%$$
$$C, mg/kg = 2.65 * 10000$$
$$= 26,500 mg/kg$$

Nitrogen requirement to treat the excess oil.

$$C/N = 150/1$$
$$26,500/N = 150/1$$
$$N = 177 mg/kg$$

$$77x2 = 354\frac{lb}{acre - 6in.},$$ since,

1 acre-6in.=2 million lb. soil
Treatment area occupies 0.05 acres. Accordingly,

$$N = 18 lbs$$

N;P;K = 4:1:1 = 18:5:5

P,K = 5lbs.

Obtain P(P_2O) and K(K_2O) requirements by using 10-10-10 fertilizer. Five lbs of fertilizer equals 11 lbs(5/0.44) of P and 6 lbs of K(5/0.83). Accordingly, reduce the calculated N by 5 lb. for the first application. Apply half the total nitrogen [9-5=4]

Using ammonium nitrate (33 percent N)

ammonium nitrate = 4/(0.33)= 12 lbs

Produced Water Remediation Calculations

Land treatment of salt contaminated soil relies on some leaching. Accordingly, the depth to usable ground water is of concern. We assume depth to usable ground water in this sample is 40 feet.

The measured and target soil EC are 127 mmhos/cm, and 8 mmhos/cm, respectively, **Table 2**

Soil Volume Required For Salinity Management

Gypsum Application Rates for ESP Remediation

ESP as a function of SAR,

$$ESP = \frac{[100(-0.0216 + 0.01475 * SAR)]}{1 + (-0.0216 + 0.01475 * SAR)}$$

Laboratory analysis shows this sandy soil has a saturated paste extract EC = 127. Based on analysis of soluble cations:

$$SAR = \frac{Na(meq/l)}{\sqrt{\frac{Ca(meq/l) + Mg(meq/l)}{2}}}$$

Millequivalents per liter are obtained by converting from milligram/liter, **Tables 2 and 3.**

Accordingly, SAR equals:

$$SAR = \frac{1864}{\sqrt{\frac{692.4 + 203.1}{2}}} = 88.1 = 88.1$$

ESP equals:

$$ESP = \frac{100(-0.0216 + 0.01475 * 88.1)}{1 + (-0.0216 + 0.01475 * 88.1)}$$

$$= \frac{127.79}{2.2779} = 56.1\,percent$$ Change in ESP required for sandy soil.

CEC for the contaminated sandy soil is 3.5 meq/100g.:

$$CR = \left[\frac{measureESP - desiredESP}{100} \right] * CEC$$

$$= \left[\frac{56.1 - 12}{100} \right] * 3.5 = 1.54$$

The gypsum addition is 1.7 tons/acre ft times the change required (CR).

Gypsum required = 1.54 * 1.7 = 2.62 tons/acre-ft.

= 262 lbs/0.05 acre-ft.
= 131 lbs/0.05 acre-6 in.

Accordingly, 131 lbs/0.05 acre-6 in. remediates the high SAR. However, this will not be adequate for correction of the high EC.

Dilution requirement for EC remediation.

EC reduction results from dilution of contaminated soil

Soil volume requirement for salinity [EC] management.
The saturated paste extract EC = 127. The target EC = 8 and the background EC = 0.8.

$$8EC = \frac{(127EC)(1089ft^3) + Xft^3 * 0.8EC}{1089ft^3 + Xft^3}$$

$$X = 17,999\,ft^3$$

Amendments

If hydrocarbon is the only consideration, apply about 5200 lb./acre, or 260 lbs for this spill area good quality hay, 12 lbs ammonium nitrate and 50 lbs 10-10-10 disk and cross disk to 6 in. to distribute the amendments. Apply the remaining fertilizer in 2 additional equal applications of (4/0.33)/2] [12 pounds] each, disking each time. Separate each application by 8 weeks. Maintain soil moisture at 50-80 percent field capacity. Eight weeks after the last fertilizer application, sample and analyze for TPH. If oil TPH>1 percent, repeat treatment. If, as in this example, produced water is involved, dilution for salt content is adequate to remediate hydrocarbon contamination.

Based on the above calculations correction of the EC dilutes the contaminated area so as to correct SAR and TPH without specific amendments. The soil dilution for EC equals 17,999 ft^3. Incorporation of this soil to 6 inches deep requires 0.88 acres.

$$\frac{[1089ft^3 + 17,999ft^3] * 2}{43560ft^2 / acre} = 0.88\,acres - 6in.$$

Table 2

Target Values To Use In Calculations

Soil Value	EC, mmhos/cm	TPH, %
Spill Area	127	3.4
Background	0.8	<0.01
Target Threshold	8	1

Table 3

Cation Millequivalents

Parameter	mg/meq	meq from saturated paste extract
Na	23	1864
Ca	20	692.4
Mg	12	203.1

Improved Drilling Technologies for Rapid Site Characterization

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Abstract

The Oil and Gas industry is required by regulatory requirements to drill numerous wells for waste site characterization and monitoring especially if there is an Underground Storage Tank (UST) involved. Cost associated with the environmentally safe completion of drilling, construction, sampling, and monitoring can be high under the regulations. Technologies that improve and reduce the costs of drilling, well completions, sampling and monitoring are needed. This would include the following: Shorter field investigation time, improved dry drilling techniques or inert drilling fluid additives to improve speed of drilling without contamination of the subsurface, better seals or casings for drilling to prevent contaminant migration and reduce costs, innovative technology for collecting downhole hydrogeological information, particularly sampling under negative pore water pressure, collecting representative lithologic and groundwater samples under hostile drilling and contamination conditions, and optimization of monitoring well networks and field analytical using a mobile Gas Chromatograph (GC). This paper discusses the use of an all terrain vehicle (ATV) with a rear mounted drilling unit, capable of drilling in hard to reach locations with minimal disturbance. Using this equipment and a portable GC, site characterization can be accomplished in one or two days under most conditions.

Introduction

Gasoline service stations and various industrial facilities have engaged in storing hydrocarbon fuels in Underground Storage Tanks (UST's). In 1988, the USEPA estimated that there were over two million UST systems (which include both the UST and integral piping) located at over 700,000 facilities nationwide. EPA judged that roughly 75 percent of these systems posed the greatest potential for leakage and environmental harm because the UST systems were made of steel without any corrosion protection.

Regulatory agencies and associated governing bodies have stipulated that subsurface contamination (groundwater and soil) must be delineated in order to contain contamination migration as well as devise a method of remediation. Methods of delineation typically involve drilling activities to procure soil and/or groundwater samples. Methods of drilling (auger rig vs probe) and associated field activities will be examined to determine the quickest and most cost effective way for site characterization.

Because of the magnitude of the drilling for monitoring wells taking place nationwide, it is important that the most cost effective method be employed. A recent study suggest the cost to clean up the nation's leaking UST's could exceed 41 billion dollars and take over 30 years as can be seen by this task significant advantages exist for probe characterization due to greater mobility and reduced monitoring well installation costs (2). Table 1 compares the use of conventional auger rig vs probe. One of the first systems of this type "The Hydropunch" has been in widespread use since the late 1980's and reduces monitoring well installation from 10-60 percent (3).

Geological Setting (The Subsurface)

Soil and groundwater probe systems offer a host of advantages over conventional auger type rig systems in certain applications. A suitable geologic setting for a probe would include unconsolidated clays, silts, sands, and fine gravel. Many probes are capable of penetrating strata in locations where a standard 2-inch split spoon sampler can be used. Sites conducive to the use of a probe tend to exhibit subsurface conditions (unconsolidated materials) that provide rapid plume migration. Plume migrations can, at times, be located beneath buildings, parks and other environmentally sensitive areas situated adjacent to the source spill. These situations lend very well to the use of a non-obstructive, non-obtrusive sampling machine (probe) for the necessary delineation (see Table 1).

Subsurface Investigations, Inc. (SI) uses an ATV unit to perform soil and groundwater probing activities during environmental site characterizations. The unit consists of a hydraulic ram and a hammer system. This system is capable of advancing 3 feet X 1 inch drill rods with relative ease through most

unconsolidated materials. The system is also equipped with a rotary bit which enables advancement through concrete and/or asphalt (4). The hammer and ram system alleviate the need for a massive weight on the rear of the probe (as a means of stabilization). This provides the probe operator with the capabilities of performing drilling activities on flooded or muddy fields, unstable terrain and other sensitive locations requiring lightweight equipment. Utilization of a probe unit also provides clients (typically) with lower cost mobilization, drilling and sampling.

Truly rapid characterization and cost savings could not be achieved without implementing quality field sampling techniques in order to locate subsequent soil/groundwater borings. The use of a Gas Chromatograph incorporated into your field lab enables the location of the horizontal and vertical extent of contamination during the initial drilling. The alternative to this particular format of characterization would include numerous site visits, therefore, increasing your mobilization charges, handling and subsequent analyses of every soil and/or groundwater sample procured, and an overall extended period of time to complete the site characterization.

Using the mobile field lab and probe provides a prospective client with real time in-field information. Isoconcentration and head elevation maps can also be produced during field activities if adequate time is provided (see examples 1 and 2). These in-field aspects of plume delineation provide the prospective client with substantial savings as well as an expedited means of completing the characterization of the clients property.

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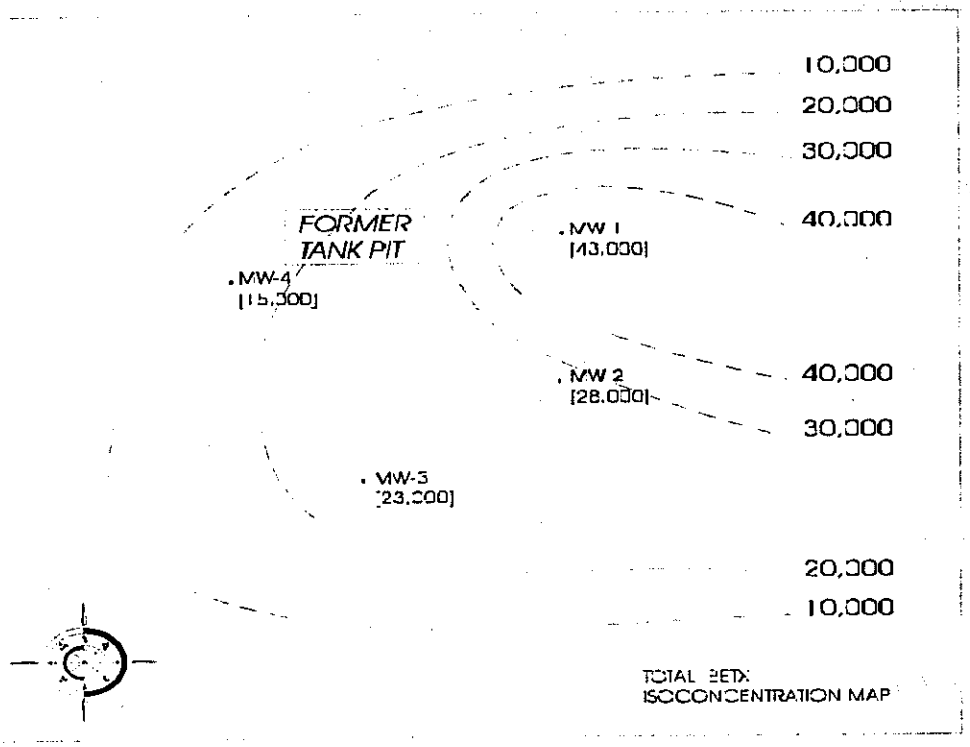
TABLE 1
COMPARISON OF MOBILE SOIL/GROUNDWATER PROBE* WITH FIELD LAB
VS. CONVENTIONAL AUGER RIG

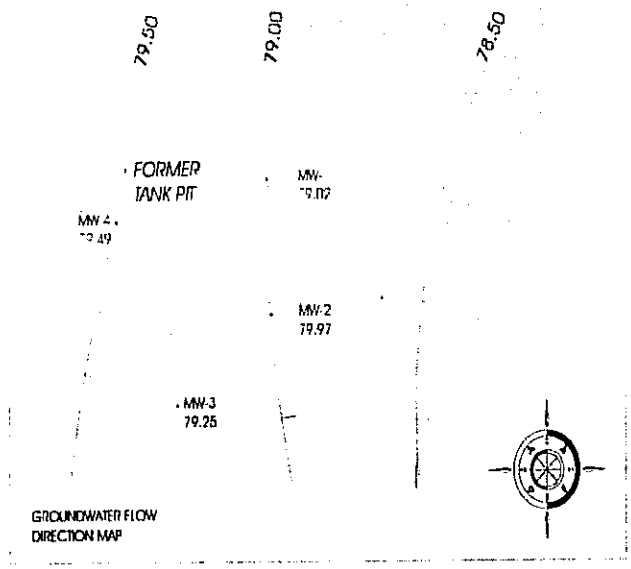
TASK	MOBILE PROBE RIG 7 - FEET BOOM	CONVENTIONAL AUGER-RIG > 12 - FEET BOOM
Mobilization		
Drilling in open field	✔	✔
Drilling around buildings	✔	Depending upon clearance
Neighborhood settings	✔	Depending upon available space
Environmentally sensitive areas such as city parks, etc.	✔	Depending upon local city ordinances
Drilling inside garages, buildings, etc.	✔	Depending upon vertical & horizontal clearances
Drilling in tight spaces between structures or around utilities	✔	Depending upon the extent of available space or proximal 'closeness' to various utilities
Associated Costs**		
Excess soil & groundwater disposal Fees	Only produce sample amounts required; no excess materials produced during probing activities	✔ Client responsible for disposal of excess material produced by auger in the event of contamination
Time Constraints		
Additional cost incurred due to 'rig up', d'con, & subsequent preparatory work between boring locations	Less time required for all preparatory work including mobilization between borings due to reduced rig and tool size	✔ Additional time constraints for mobilization and d'con between borings are associated with auger rig due to increased rig and tool size
Analytical		
On - site lab capabilities in order to expedite delineation process	✔	extended waiting period for delineation due to sample handling & excessive turn-around time of conventional lab

* Assuming unconsolidated materials in the subsurface, and probe dimensions of less than 48 - inches width x 75 - inches height
** Assuming only costs above and beyond drill costs. Probe costs have previously been substantiated as cheaper on a per-foot basis

EXAMPLE 1



EXAMPLE 2



Application of Composting Techniques to Enhance the Bioremediation of Soils Contaminated with Refined Petroleum Products

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Abstract:

Increasingly restrictive regulations and ever increasing costs are driving the search for environmentally sound, cost effective, on-site techniques for the remediation of petroleum contaminated soils. One such possible technique utilizes bulking materials to aid in a biological degradation of the petroleum in a composting process.

Bench scale research has been conducted utilizing composting techniques, employing wood chips as a bulking agent, to remediate soils contaminated with refined petroleum products. The research effort specifically focussed on gasoline contamination as might result from a pipeline or storage tank release. Progress of the remediation was monitored by regular measurement of total petroleum hydrocarbon concentration, and biological activity in the soil. The effects of various moisture levels (35 percent, 15 percent and natural) and nutrient levels on the degradation rate were also studied. To provide experimental control, a system modeling a typical land farm treatment and a biologically inhibited compost system were included in the study.

This paper will report the results of this research and the applicability of this remediation technique to the clean up of soils contaminated by refined petroleum products. Specifically the purpose of this research was three fold:

1) To investigate the applicability of composting as a method of remediation of soils contaminated with gasoline.

2) Investigate the effects of environmental variables (moisture and nutrients) on the biodegradation of the gasoline.

3) Compare the remediation potential of composting to land farm treatment for gasoline.

INTRODUCTION

BACKGROUND

Many years of America's reliance on fossil fuels has resulted in hydrocarbon contamination of soils and groundwater at thousands of sites across the country. These sites include: industrial areas contaminated with lubricating oils, refineries, gasoline stations, and fuel and chemical storage facilities. Transportation related spills, such as pipeline incidents, constitute yet another source of contamination which presents the unique situation where the responsible party is often not the site owner. Soil contamination at many sites has been largely ignored or relegated to a lower priority due to the slower rate at which soil contaminated areas expand and impact adjacent properties, as compared to groundwater contamination. While some of these contaminated sites may have existed for many years, media attention and increasing public awareness has resulted in site owners and responsible parties aggressively seeking to discover effective remediation alternatives for many of these soil contamination sites. Regulatory requirements, economics, site geology, accessibility, future liability, site ownership, and time are just some of the issues that must be addressed when developing a soil remediation strategy.

The major focus of this research is on the remediation of soils contaminated by recent releases of refined petroleum products from pipelines. As a result of regulatory requirements to remove the contamination and lack of ownership of the site, pipeline spill contamination must be addressed in an extremely timely manner following the discovery. Thus the age of contamination from pipeline releases is most likely measured in weeks rather than years as may be the case with other sites. Pipelines are typically constructed in

areas where they will impact the fewest number of people and in as straight a line as possible. These construction priorities result in many locations where future accessibility becomes a major issue. Lack of roads, swampy ground, wet lands and other geographical features make access a major factor in choosing a clean up strategy. Accessibility, increasingly restrictive regulations, and ever increasing costs are driving the search for environmentally sound, cost effective, on-site techniques for the remediation of these petroleum contaminated soils. (1)

On-site bioremediation, in its most basic form, can be defined as a process where the contaminated site is disturbed to allow contacting of the contaminants with oxygen or other electron acceptors, nutrients and/or microorganisms. Advantages of on-site bioremediation are better control of environmental conditions (oxygen, temperature, moisture, etc.), better control of nutrient application, and shorter time requirements. (1) The ability to control the environmental conditions is directly related to biodegradation rates and ultimate contaminant removal efficiency. (2) (3) One possible on-site remediation technique, composting, utilizing bulking materials to aid in the biological degradation of the petroleum is the subject of this paper.

Bench scale research of composting techniques, employing wood chips as a bulking agent, was conducted to determine the potential applicability of this type system to the remediation of soils contaminated with refined petroleum products. The research effort specifically focussed on gasoline contaminated soil. Progress of the soil remediation was monitored over time by measurement of total petroleum hydrocarbon concentration and biological activity in the soil. Additionally temperature, pH, nutrient levels and oxygen content were periodically measured. Variables studied during this research included moisture levels (35 per cent, 15 per cent by weight and natural), and nutrient levels. To provide experimental control a system modeling a typical land farm treatment and a biologically inhibited compost system were included in the study.

A number of researchers have studied various aspects of the aerobic biodegradation of refined petroleum products. Research conducted by Aamand et al., (4) Ridgeway et al., (5) Fredrickson et al., (6) and others has shown that refined petroleum fractions are readily degradable by indigenous microorganisms. Other Research conducted by Wang et al., (7) Harder and Hopner, (8) Song et al., (9) and Song and Bartha, (10) studied the effects

of moisture, nutrient levels, soil type, and refined product type on the biodegradation process. The rate of biodegradation and the ultimate removal efficiencies were also studied. The work shows both the feasibility of on-site remediation as well as pointing out some of the advantages. The common element in all the research mentioned above is the successful bioremediation of the refined petroleum fractions.

Composting as a technique for enhancing the biodegradation of various organic material has been researched for over two decades. Publications by MacGregor et al., (11) and Feinstein and Morris, (12) provide detailed discussions of the microbiology involved in the process, nutrient requirements, operation and the commercial success of composting of municipal wastes. Even with this knowledge application of composting to petroleum compounds is only a recent innovation. Fyock et al. (13) presented a paper which discussed a successful pilot scale project to remediate crude oil sludges. This project represents one of the first documented efforts to apply the technology to petroleum wastes.

MATERIALS AND METHODS

A sandy soil used in this study was acquired at the site of an actual pipeline release. The biological remediation of this soil was conducted in bench scale research. The soil was contaminated with gasoline as a result of the release. Analytical techniques discussed below were used to monitor the progress of the remediation process.

SOIL BACKGROUND AND ACQUISITION

The research was developed around the remediation of a single soil contaminated with gasoline. The soil for the research was taken from a point down gradient of the pipeline, at a depth of two to three feet below the surface. This location was believed to have experienced less weathering and volatilization than up gradient soils and those at the ground surface. The spilled product was reported to be primarily unleaded gasoline with a reid vapor pressure in the range of 7.4 to 10.4 pounds per square inch (psi). The spill site was approximately eight months old at the time the soil was obtained. The soil was placed in plastic bags and sealed in buckets for transport and storage.

A sample representing a composite of all the buckets was taken and analyzed to determine the carbon, nitrogen and phosphorus content in milligrams per kilograms of soil. These data were then related as the Carbon to Nitrogen to Phosphorus ratio (C-N-P). The initial C-N-P ratio established the basis for determining the necessary additives used in preparing the bench scale biological systems.

PREPARATION OF COMPOST AND CONTROL SYSTEMS

Preparation of the static pile compost models was conducted on February 3, 1993. Eight styrofoam boxes, having a volume of approximately 0.02 cubic meters each, were used to contain the static pile compost systems and one land farm system as a control. The styrofoam was used to model the insulating effect that would exist in a full scale compost pile or land farm system. Changes in temperature due to microbial activity cannot be seen in compost systems less than about one cubic meter in size due to lack of mass to hold in heat (14). Each system was initially established with 8.57 kilograms (kg) of sandy soil. Wood chips were added to the seven compost systems based on a volume of soil to volume of wood chips ratio of 1 to 2. This volume of wood chips added 1.45 kg to the seven compost systems for a total of 10.02 kg. The wood chips used were dry, softwood, saw mill shavings. The typical wood chip was 1.9 centimeters by 1.3 centimeters and showed no visual evidence of any decomposition.

The primary variables investigated during the research were moisture and nutrient levels. Two moisture levels and two nutrient levels were established for study. The two moisture levels were 35 per cent and 15 per cent moisture by weight. The nutrient levels studied were represented by C-N-P ratios of 100-25-3 and 100-10-3. Both nutrient levels were combined with each moisture level resulting in the four primary compost system models. These four systems will be referred to as 35 high nitrogen, 35 low nitrogen, 15 high nitrogen and 15 low nitrogen. The remaining four of the eight systems were control systems and consisted of: a land farm model with a 15 per cent moisture level and no bulking material; a 35 per cent moisture compost system and a 15 per cent moisture compost system both of which were biologically inhibited with Fisher Scientific Reagent Grade mercuric chloride ($HgCl_2$) in a 2 per cent solution; and a compost system into which nothing was introduced

other than the soil and wood chips (i.e., no nutrients, water or microorganism sources). These four control systems are referred to as the land farm, 35 inhibited, 15 inhibited, and natural compost, respectively. Moisture levels in the various systems were determined initially and adjusted using tap water. Nutrient content was adjusted in the 100-25-3 (high nitrogen) systems by adding Fisher Scientific Reagent Grade potassium nitrate (KNO_3) as a nitrogen source. The naturally occurring nutrients were utilized for the 100-10-3 (low nitrogen) systems.

The four primary compost pile models and the land farm model were each inoculated with three sources of microorganisms to help accelerate the initial microbial growth. The three sources included: 50 milliliters (ml) of mixed liquor from a refinery activated sludge treatment system, 20 grams (gm) of a soil which was known to have been contaminated with petroleum hydrocarbons for several years, and 2 gm of Ringer. Ringer is a commercial compost system starter consisting of nonpathogenic cellulose degrading and nitrogen fixing micro-flora. Table I details the specific composition of each of the eight systems utilized in this phase of the research.

MEASUREMENTS AND ANALYTICAL DETERMINATIONS

Several parameters were measured during the course of the research for use as indicators of the progress of the remediation process and/or biological activity. The parameters include: temperature of the system, pH of the system, oxygen content inside the system, moisture content, total petroleum hydrocarbon content (TPH), fluorescein diacetate hydrolysis (FDA), total organic carbon (TOC), nitrogen content(N), and phosphorus content(P).

DIRECT MEASUREMENTS ON THE SYSTEMS

Temperature, pH and oxygen content within the system were measured with direct reading instruments on the system or samples from the systems. Temperature of the systems was measured periodically in degrees fahrenheit. The pH of the various systems was determined by mixing a 10 gm sample of the system with 100 ml of distilled water. The soil and water were stirred for several minutes utilizing a magnetic stirrer. The pH of the resulting mixture was then measured directly with a Cole

Parmer Model 5996-50 pH meter. The oxygen content of the systems was measured with a Scott Model S105A combustible gas, oxygen monitor. A probe, attached to a hand operated aspiration adaptor, was placed near the middle of the system and at a depth within the lower third of the system. The oxygen content was then read directly as percent oxygen in the air contained in the system.

ANALYTICAL DETERMINATIONS

The moisture content of each system was determined by weighing a sample of each system, drying the sample, then again weighing the sample. The percent moisture was then calculated based on the decrease in mass due to the drying process

Total petroleum hydrocarbon (TPH) concentration was determined utilizing a Perkin Elmer Model 8500 Gas Chromatograph (GC) coupled to a Perkin Elmer LSC-2 Liquid Sample Concentrator (purge and trap). The GC temperatures and ramp rates used were consistent with the United States Environmental Protection Agency Standard Method 8020 SW - 846. (15) Samples from the various systems taken at seven to fourteen day intervals were evaluated by placing a known weight of sample, 1 to 2 grams, in 5 ml of reverse osmosis (RO) filtered water and mixing. The mixing was done by shaking the sample and water for about one minute. The mixture was evaluated using the purge and trap and the GC mentioned above. The TPH content was then calculated by evaluating the ratio of the area under the sample chromatogram to that of the standard chromatogram.

Spectrophotometric measurement of the hydrolysis of FDA was used to provide a method for the determination of the microbial activity in the soil. More specifically, FDA hydrolysis was used to measure the activity in one system relative to another and as an indication of the change in activity in a single system. FDA is hydrolyzed by various enzymes resulting in the enzymatic conversion product fluorescein. The fluorescein can be visualized within the cell by fluorescence microscopy and can be quantified by fluorometry or spectrophotometry (16).

For purposes of this particular research a standard method of measuring the microbial activity using FDA hydrolysis was developed and adhered to throughout the project. In preparation for the measurement of the FDA hydrolysis a stock solution of Sigma Chemical Company Reagent Grade FDA in acetone was prepared at an FDA

concentration of 2 mg per ml of acetone. A soil sample weighing 1.05 gm was placed in a 150 ml beaker with 0.5 ml of a stock FDA solution and 100 ml of a 60 millimolar (mM) sodium phosphate, 7.6 pH, buffer. The 60 mM sodium phosphate buffer was prepared from Fisher Scientific Reagent Grade sodium phosphate crystals and distilled water. The mixture was placed on a magnetic stirrer for 30 minutes. Following the mixing the solution was allowed to stand at room temperature for 1.5 hours and then centrifuged at 6000 revolutions per minute (rpm) for ten minutes. The resulting liquid was placed in a direct reading Hach DR/3 Spectrophotometer. The absorbance of light was measured at 490 nanometers. The spectrophotometer was calibrated before use with a solution containing 0.5 ml of the stock FDA solution and 100 ml of the 60 mM sodium phosphate buffer.

The original TOC of the soil was determined initially using a titration methodology developed by Gaudette et al. (17). The measured TOC represents both soil TOC and contaminant. This determination was done to help establish a base C-N-P ratio and was not used as a parameter to monitor the progress of the various remediation processes.

The determination of the N and P concentrations was conducted on the original soil to determine the necessary additions to reach the desired C-N-P ratios. In both cases the standard EPA spectrophotometric methods as outlined in SW-846 (15) for analysis of total nitrate as nitrogen and total phosphorus were utilized. One deviation from the EPA standard method, known as the cadmium reaction method, was employed in the case of the nitrogen. That deviation was the extraction of nitrogen from the soil sample for 1 hour using a potassium chloride solution. A Hach DP/3 Spectrophotometer was employed to complete the determination using the Hach Nitro Ver-5 prepared reagents and direct reading methodology. To determine the phosphate concentration, the EPA standard method known as the ascorbic acid method was employed. A soil sample was first digested with persulfate and sulfuric acid. The Hach DP/3 Spectrophotometer was again used for the determination utilizing the Hach Phospho Ver-3 prepared reagents and direct reading methods.

RESULTS AND DISCUSSION

As outlined above, this research centered on the remediation of a sandy soil contaminated with unleaded

gasoline. The original organic carbon content of the soil, plus the carbon content resulting from the gasoline, was determined to be 736 mg/kg while the nitrogen and phosphorus concentrations were determined to be 69 mg/kg and 20 mg/kg, respectively. These results indicated a C-N-P ratio of 736-69-20. Reduced to a standard ratio with C equal to 100 the C-N-P ratio becomes 100-9.4-2.7. The two nutrient ratios originally designed for this phase one investigation were 100-10-1 and 100-25-3. However, it was decided the natural nutrient ratio that the soil exhibited would be used for the low nutrient case, instead of 100-10-1, and that only the nitrogen level would be increased for the high nutrient case. An additional 115 mg/kg of nitrogen was added in the form of KNO_3 to two of the compost systems bringing the C-N-P ratio to 736-184-20 or 100-25-3. Addition of nutrients was done only once, during initial preparation of the systems. The original moisture content of the contaminated soil was determined to be 7 per cent. Table I summarizes the initial composition of the eight systems prepared for the research. The tops of the styrofoam boxes were left open to allow for the natural volatilization of moisture and product to occur. The eight systems were kept inside where the ambient temperature was maintained between 40 and 75° F. The lower temperatures occurred during weekends when heating was turned down. The duration of this first phase of the research was 45 days. The eight systems were thoroughly mixed and aerated by turning the soil with a garden trowel for five minutes six times during the study. Each system was aerated when prepared then subsequently on days seven (7), thirteen (13), twenty-one (21), thirty-one (31) and forty-five (45). No attempt was made to maintain nutrient levels at the initial C-N-P ratios. The moisture levels in all the systems, except the natural compost system, were maintained by additing tap water as needed prior to each mixing. The moisture content of the natural compost system decreased from 7.0 to 1.7 percent during the investigation.

The primary data collected are plotted on graphs depicting changes in the values versus time for each of the systems. Figures 1 through 8 are the plots of this data. The pH of the various systems remained relatively constant during the investigation ranging from 6.6 to 7.3. Final phosphorus content in all eight systems exhibited a decrease. The phosphorus content in the natural compost system and the inhibited systems decreased on the order of 7 mg/kg while the decrease in the other systems ranged from 5.6 to 2.6 mg/kg. This result may be due to some additional phosphorus being added with the Ringer.

Table I

System Compositions

System	C-N-P	Soil (kg)	Wood Chips (kg)	Moisture (Weight) (Percent)	N. Concentration (mg/kg)	Ringer (gm)	Activated Sludge (ml)	Long Time Contaminated (gm)
35 High Nitrogen	100-25-3	8.57	1.45	35	184	2	50	20
35 Low Nitrogen	100-9.4-3	8.57	1.45	35	69	2	50	20
15 High Nitrogen	100-25-3	8.57	1.45	15	184	2	50	20
15 Low Nitrogen	100-9.4-3	8.57	1.45	15	69	2	50	20
Land Farm	100-9.4-3	8.57	-0-	15	69	2	50	20
Natural Compost	100-9.4-3	8.57	1.45	7	69	0	0	0
35 Inhibited	100-9.4-3	8.57	1.45	35	69	(Biologically inhibited with 2 per cent $HgCl_2$ by weight solution in the added water)		
15 Inhibited	100-9.4-3	8.57	1.45	15	69	(Biologically inhibited with 2 per cent $HgCl_2$ by weight solution in the added water)		

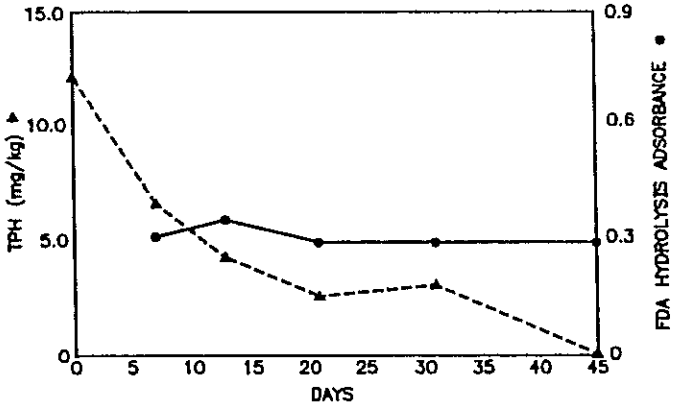

Figure 1: FDA hydrolysis and TPH data from the 35 per cent moisture, low nitrogen system.

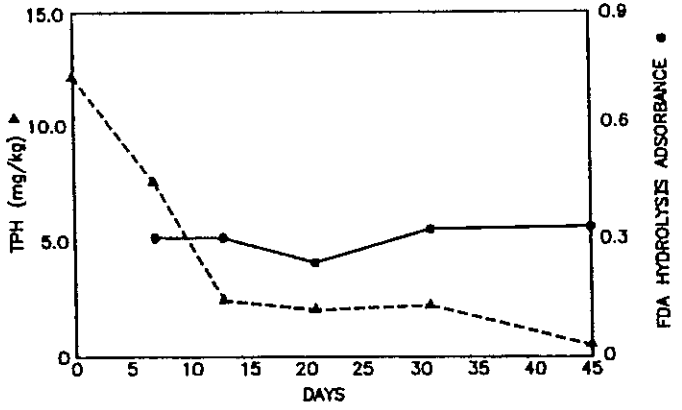

Figure 2: FDA hydrolysis and TPH data from the 35 per cent moisture, high nitrogen system.

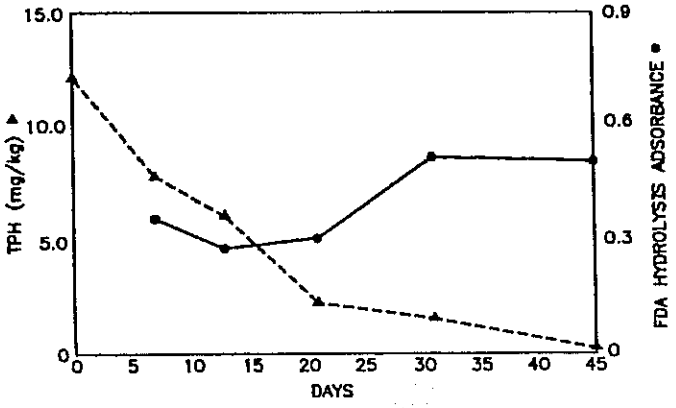

Figure 3: FDA hydrolysis and TPH data from the 15 per cent moisture low nitrogen system.

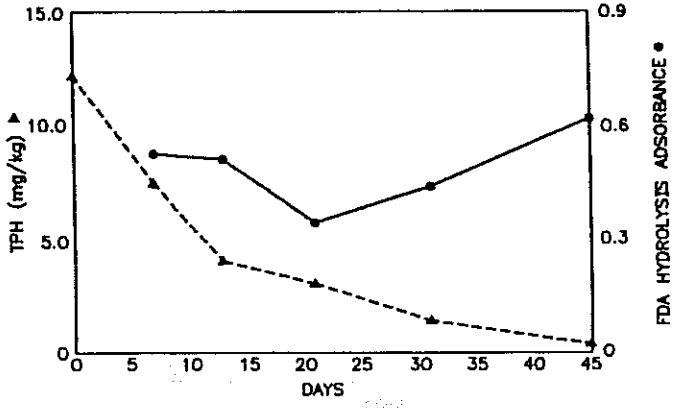

Figure 4: FDA hydrolysis and TPH data from the 15 per cent moisture high nitrogen system.

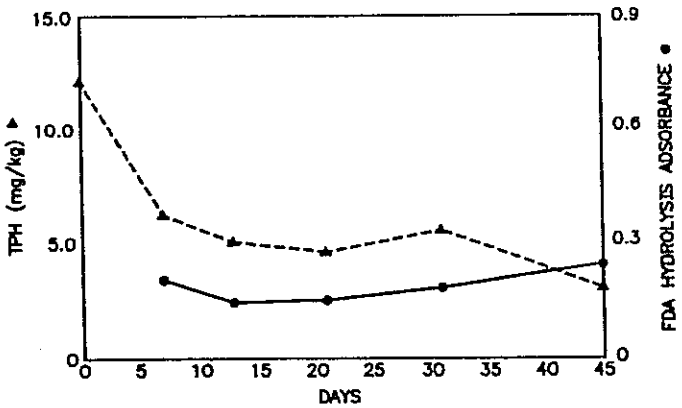

Figure 5: FDA hydrolysis and TPH data from the 15 per cent moisture inhibited system.

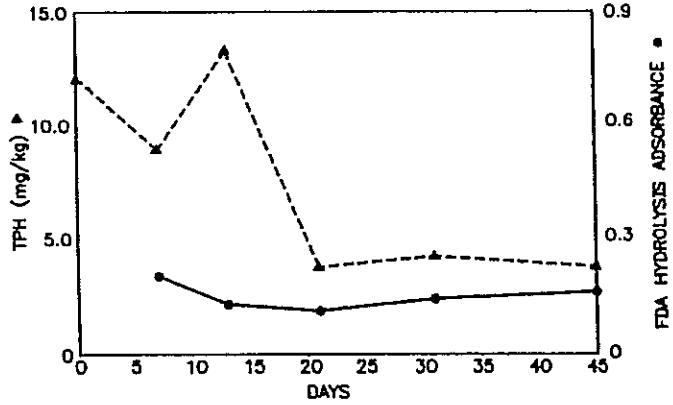

Figure 6: FDA hydrolysis and TPH data from the 35 per cent moisture inhibited system.

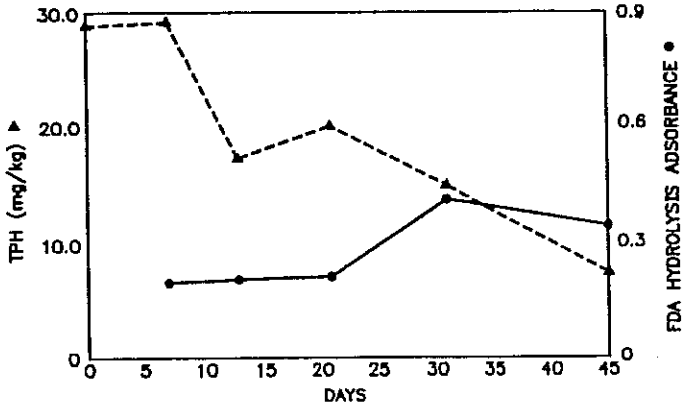

Figure 7: FDA hydrolysis and TPH data from the land farm system.

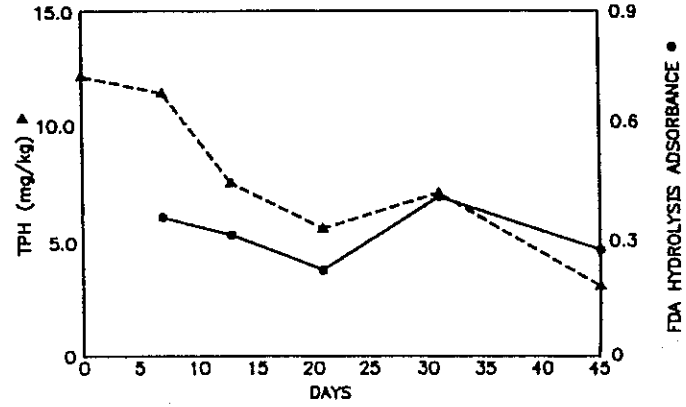

Figure 8: FDA hydrolysis and TPH data from the natural compost system.

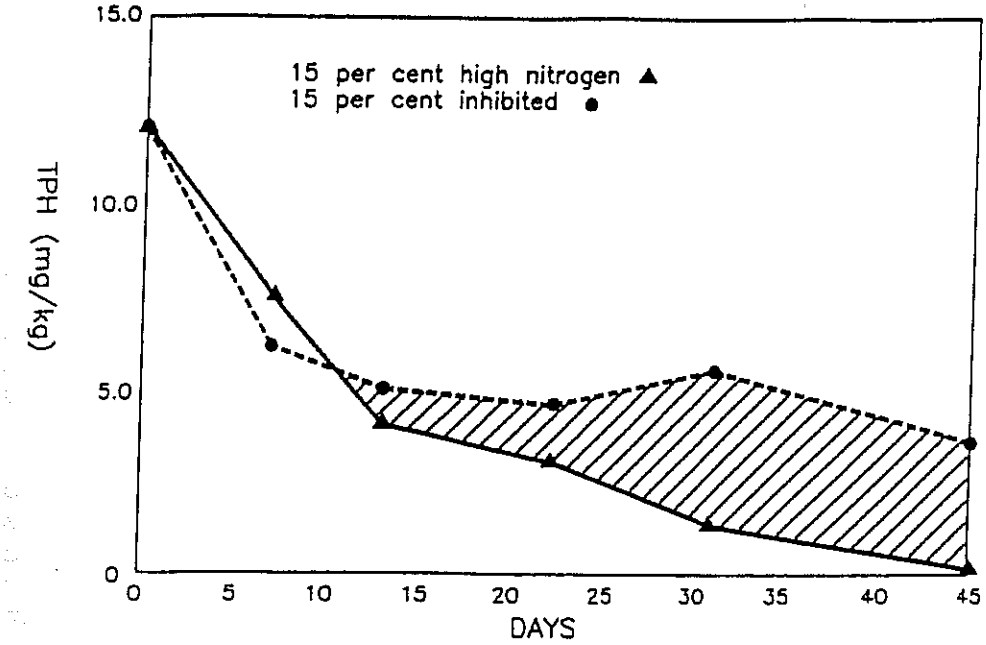

Figure 9: Comparison of the 15 per cent high nitrogen system to the 15 per cent inhibited system.

In reviewing the plotted data one of the first items of interest is the difference between the initial TPH of the land farm model (28.9 mg/kg) and the compost systems (12.1 mg/kg). This apparent inconsistency is a direct result of all the handling of the soil in the lab preparing the systems and the additional mixing involved in preparation of the compost piles. This handling leads to volatilization of light fractions, which explains the difference between the compost and the land farm. Volatilization loss of gasoline has been found to be on the order of 85 per cent after 24 hours of exposure to the atmosphere. (18) This potential for volatilization in addition to the additional agitation of the compost systems explains the inconsistency in concentration between systems.

The plotted data show that in all eight cases the TPH concentration decreased over the forty-five days. The apparent decreases in the two biologically inhibited controls, the land farm system, and the natural compost system were all on the order of 70 to 75 per cent. The four compost systems that were supplied nutrients and moisture showed decreases on the order of 95 to 99 per cent. Figure 9 is a plot comparing the 15 per cent high nitrogen system to the 15 per cent inhibited control. This plot clearly shows the additional hydrocarbon removal in the biologically encouraged (provided nutrients and moisture) systems versus the inhibited

control. In general, this result is consistent with the results reported in the research conducted by Wang et al. (7). In that research, a reduction in the lower molecular weight hydrocarbons from both treated and untreated soils was noted after two weeks. At the end of twelve weeks of study the untreated soils had remaining contamination of 12.5 to 32.5 per cent while the treated soils had been remediated below detection limits. Figure 9 shows a similar trend with both systems exhibiting a reduction in contamination during the first thirteen days. After the first two weeks the treated system continued to decline while the inhibited control system's decline rate stabilized at a slower rate. Song et al. (9) noted that the half-life of gasoline differed only slightly between biologically encouraged and inhibited controls. The half-life of the gasoline in the two systems shown in Figure 9 differ only by 1.5 days. The apparent half-life exhibited by the 15 per cent high nitrogen system was 9.5 days while the 15 per cent inhibited system was 7 days.

The existence of biological activity is confirmed by the FDA hydrolysis data. The FDA hydrolysis absorbance ranged from 0.2 to 0.62 for the non-inhibited systems while the biologically inhibited systems remained below 0.24 as shown in Figures 1 through 8. It follows from these data that the incremental contaminant reduction exhibited in Figure 9 is the result of biological degradation and that the composting system does provide a viable system where biodegradation can take place.

A comparison of the results of the natural compost system to the results of the remaining four biologically enhanced compost systems where moisture was added and maintained lends insight into the importance of water to the biodegradation process. The natural compost system resulted in gasoline contamination reduction similar to the reductions observed in the inhibited systems. The remaining gasoline after 45 days was 3.1 mg/kg versus 3.0 mg/kg and 3.7 mg/kg for the two inhibited systems. The FDA hydrolysis absorbance data ranged from 0.23 to 0.42 for the natural compost system. The plot of the data, however, more closely resembles that of the biologically inhibited system plots. The 0.42 value appears to be an anomaly in this case. The difference between the natural compost system and either the 35 low nitrogen system or the 15 low nitrogen system was moisture. The natural compost system initially had a moisture content of 7.0 percent and was allowed to dry out. The other two systems were given supplemental moisture initially and the higher moisture levels were maintained during the 45

day period. In research conducted by Harder and Hopner (8), similar results were observed. The Harder and Hopner (8) data indicated that increased moisture leads to increased degradation. The data obtained in this study mirrors those results when the natural compost system is compared to the higher, 15 percent and 35 percent, moisture systems.

Comparison of the 35 percent moisture systems to the 15 percent moisture systems does not lead to a conclusion relating to effect of nutrient level (i.e. 100-25-3 versus 100-9.4-3) or moisture level on the biodegradation process. At both moisture levels the lower nitrogen level system did exhibit a lower final contaminant concentration. The residual TPH concentration in the 35 percent high nitrogen system was 0.5 mg/kg compared with 0.1 mg/kg for the low nitrogen system. In the 15 percent moisture systems, the residual TPH concentrations were 0.4 mg/kg in the high nitrogen system and 0.2 mg/kg in the low nitrogen system. This result, however, is not supported by any rate of decline, FDA hydrolysis, or other data that would lead to a conclusion that one nitrogen level was more effective than the other. Based on the data one can only conclude that both the 100-25-3 and the 100-9.4-3 systems provide adequate nutrients to support the biological process. Likewise the comparison of the four biologically encouraged compost systems for a relationship between the supplied moisture levels and biodegradation rate or ultimate contaminant level is inconclusive. One can only conclude that both moisture levels were sufficient to encourage the process. The apparent effect of the bulking agent on the systems can be seen in a comparison of the four biologically encouraged compost systems versus the land farm. The land farm system, while showing FDA hydrolysis absorbance and microbial activity resulted in only a 73 percent contaminant removal compared to the 95 percent or greater removal in the compost systems. From this data TPH removal from the land farm system appears to be primarily volatilization. The most direct comparison is of the land farm to the 15 percent low nitrogen compost system. In this case the compost system, 98 percent removal, significantly out performed the land farm system. It is theorized that this difference in performance was due to lower oxygen levels in the land farm. The lower oxygen levels would be directly related to the lesser degree of mixing done on the land farm system prior to sampling and lack of bulking material.

One final observation from the data is the lack of temperature change due to increasing microbial activity. The work of Fyock et al. (13) on petroleum sludges would

indicate that thermophilic bacteria played a major role in this degradation. In that work during the pilot scale phase the temperature was monitored daily and mixing was required to maintain the temperature of the compost pile at less than 135° F. Feinstein and Morris (12) also indicate that elevated temperatures are to be expected in a compost system. During the course of this research no such increases occurred. The result is presumably due to the difference in scale of the bench scale versus pilot scale research.

SUMMARY AND CONCLUSIONS

The stated purpose of this research was three fold:

1) To investigate the applicability of composting as a method of remediation of soils contaminated with gasoline.

2) Investigate the effects of environmental variables (moisture and nutrients) on the biodegradation of the gasoline.

3) Compare the remediation potential of composting to land farm treatment for gasoline.

The research effort was in fact successful in addressing these issues and providing answers to these questions. The composting systems were successful in establishing viable microbial systems which biologically degraded and removed the contaminant present. While volatilization of the gasoline was the primary removal mechanism, 20 percent or more of the contamination was removed from the soil biologically. In a full scale system where a lesser per cent of the composting material should be exposed to the atmosphere and where higher molecular weight, less volatile, contaminates are present volatilization will become a less important mechanism.

The research provided insight into the effects of nutrient level and moisture on the composting systems. The nutrients, while necessary at a minimum level to support the microbial growth in the system, do not appear to enhance or hinder the process beyond that point. The C-N-P ratios used throughout the research proved to be more than adequate to encourage the microbial processes. Moisture does play a significant role in the efficiency of the composting system in a similar manner as shown by Harder and Hopner (8). Higher moisture levels were shown to have a positive effect on the compost remediation

system. The relative short duration and the effects of volatilization, however, tended to mask the effects.

During this research the compost systems more rapidly decreased the contaminant concentrations than did the land farm system. Based on the results seen if applied to a full scale application the composting system would remediate a soil contaminated with gasoline faster than land farming. The land farm system has two primary disadvantages when compared to the composting system. The first is the lack of pore space, or bulk, to provide storage for oxygen and second is the need to spread the contaminated soils relatively thin, 18 to 24 inches deep, over a large area as compared to a compost pile. The land farm advantages are the absence of required specialized mixing equipment and saving the cost of the bulking agent.

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NOMENCLATURE

C	carbon
cm	centimeter
C6	six carbon hydrocarbon
C9	nine carbon hydrocarbon
° C	Degrees centigrade
° F	Degrees fahrenheit
EC_{50}	effective concentration to 50 per cent of a population
FDA	fluorescein diacetate
GC	gas chromatograph
gm	gram
$HgCl_2$	mercuric chloride
KNO_3	potassium nitrate
kg	kilogram
l	liter
mg/kg	milligrams per kilogram (ppm)
ml	milliliter
mm	millimeter
N	nitrogen
P	phosphorus
ppm	parts per million (mg/kg)
TPH	total petroleum hydrocarbons
ul	microliter

Analytical and Statistical Approaches to Validate Biological Treatment of Petroleum Hydrocarbons in Soil

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ABSTRACT

A site in southern California, containing 50,000 cubic yards of petroleum contaminated soil, was remediated using land treatment. By using a combination of soil screening and land treatment, the total petroleum hydrocarbon content was reduced to less than the clean-up standard of 1,000 mg/kg. Initial contaminant concentrations ranged between 4,000 and 5,000 mg/kg after screening to remove large globules of tar and pieces of asphalt. Biological treatment time was less than eight months per lift. Simple parametric and nonparametric statistical methods were applied to the results obtained from soil testing. Multiple analytical methods were used to determine the type of residual hydrocarbon and the relative environmental risk associated with the residual contamination. This combination of physical segregation, land treatment, and statistical and analytical methods resulted in soil remediation and permission to use the soil on site without restriction.

INTRODUCTION

Bioremediation of petroleum contaminated soil can be a very successful technology provided that reasonable performance standards are established(1-6). In general high molecular weight hydrocarbons are more resistant to biodegradation than lower molecular weight hydrocarbons. Very heavy petroleum hydrocarbons, such as asphalt, are recalcitrant to biodegradation. In cases where a broad range of hydrocarbons is present in soil, remediation standards should be set based on toxicity, mobility, and the potential for human and ecological endangerment. Using this approach, gasoline and fresh diesel range hydrocarbons, molecules with 25 to 30 carbon atoms and less, are identified as the most offensive. They are also the most biodegradable. The biological treatment (land treatment) of excavated soil containing gasoline and diesel range hydrocarbons has been applied at numerous sites during the past decade.

Land treatment of excavated soil involves the application of fertilizer, tilling or plowing to aerate the soil, and irrigation(1, 6). Soil pH may also need to be adjusted during the remediation process(6). Land treatment is often performed by placing the soil within a containment facility. This may be as simple as constructing a berm around the treatment area. The primary purpose of the containment berm is to control water run-on and run-off. More elaborate treatment cells have an impermeable liner and a drainage system below the contaminated soil. This paper describes the application of land treatment to soil contaminated with a broad spectrum of hydrocarbons including asphalt-like hydrocarbons. In addition to an aggressive treatment plan, the analytical and data evaluation plan defined the type, concentration, and distribution of residual hydrocarbons present after remediation. This approach lead to permission to use the treated soil on site as clean fill.

SITE DESCRIPTION

The subject site, located in southern California, was purchased a few years ago for eventual use as the site for a large frozen food locker and distribution point. Previously, the site housed a coke plant. During past years, a significant part of the site was also paved with asphalt. During the interim from purchase to construction, one acre of the site was leased unwittingly to an unscrupulous business man who illegally imported nearly 40,000 cubic yards of petroleum contaminated soil. In addition to illegally importing and stockpiling soil on the one acre of leased land, the operation expanded to ultimately cover most of the 17 acre site. The contaminated soil was abandoned when the operator apparently went underground.

At this point, the local water board and the health department intervened. Following characterization of the site, the regulatory agencies determined that the site did not meet environmental standards. The owners were left with the responsibility and cost for remediation prior to execution of their business plans for the site.

LAND TREATMENT DESIGN AND OPERATION

A complete site assessment was conducted to determine the extent of contamination. A total of seventeen soil borings were completed to a depth of 40 feet. Contaminated ground water was encountered at 70 feet; however, the contamination was determined to be from an upgradient source. Soil stockpiled on site was characterized for total petroleum hydrocarbon (TPH) content using U.S. EPA Method 418.1. Initial TPH concentrations averaged 4,000 to 5,000 mg/kg with several samples containing more than one percent TPH. Soil borings indicated surface contamination to a depth of six inches. Additionally, the soil was also examined for factors that are known to affect the successful execution of bioremediation. These parameters include soil pH, the residual nutrient content, the total bacterial population size and the number of hydrocarbon-degrading bacteria, and the ability of indigenous bacteria to respond to oxygenated, nutrient-amended conditions was also determined.

Table 1 summarizes the results of the bioremediation assessment. As indicated site conditions were generally conducive for bioremediation. An adequate microbial population was present and the population responded to oxygenation and nutrient addition by increasing in density by 10 to 1,000-fold. The results of the laboratory assessment indicated that bioremediation was a viable treatment technology for on site soil remediation.

Based on the relative degradability of TPH, and the favorable results obtained from the bioremediation assessment, land treatment was recommended as a cost effective and efficient approach for treating the subject soil. Prior to implementing the bioremediation plan, the top six inches of soil was scraped off the entire site and stockpiled. The total soil requiring treatment was 50,000 cubic yards. The soil was screened using a one inch sieve to remove concrete, rebar, miscellaneous construction debris, and large pieces of asphalt and tar. Material removed by screening was hauled off-site for recycling. Following screening, approximately 38,000 cubic yards of soil remained on site for remediation.

Because the soil was already segregated into discrete piles, the land treatment system was designed to isolate soil with higher TPH concentrations into separate treatment cells. Six treatment cells were defined by short soil berms covered with plastic. The volume and location of each cell are shown in Figure 1. The six cells covered nearly the entire 17 acres and contained 30,000 cubic yards of soil. Soil was placed two feet deep in each cell. A seventh cell was constructed and the remaining 8,000 cubic yards of soil was placed into treatment after combined cell 2/3 was closed.

The construction of several small cells facilitated water management during the winter. This became a critical issue because of the unusually high amount of rainfall experienced during the winter of 1993. Portable containment tanks were used to hold excess rainwater until it could be reapplied as irrigation water in the cells. This action successfully prevented the discharge of contaminated water from the site.

Soil in the land treatment cells was aerated using agricultural tilling equipment. The 24 inch soil lift was turned each week, weather permitting, with a five bottom turning plow. The top 12 inches was also tilled with a tractor-powered roto-tiller. The adequacy of this tilling regime was determined by periodically measuring soil respiration.

To determine the effectiveness of soil aeration and to define the tilling frequency, semi-quantitative soil respiration tests were conducted. Immediately following tilling, a plastic container was driven bottom-up into the soil. A septum in the bottom of the container was used as a sampling port for measuring soil gas oxygen and carbon dioxide. Daily soil gas samples were collected. The sampling system was left in place until the next tilling event. During the one week tilling cycle, a few percent of the soil gas oxygen was consumed. This observation indicated that the soil was adequately aerated by the tilling procedure and that oxygen was not completely consumed between tilling events and thus the tilling frequency and method was considered acceptable to maintain adequate soil aeration.

The field respiration tests were not conducted with the accuracy or frequency to quantitate bioremediation. With slight modifications to the respiration measurement procedure, the mass of petroleum biodegraded and the rate of degradation could be calculated. However, during this project the sole purpose of the respiration test was to evaluate the effectiveness of operation and maintenance procedures for aerating the soil.

Soil moisture was adjusted based on visual inspection. During most of the year, irrigation was required on a daily basis to maintain soil moisture and control dust. Water canons and tanker trucks were used to deliver water to the cells and access roads.

Nutrients were added in the form of agricultural-grade urea and super-phosphate. Ammonia concentration in the soil was determined during weekly field analyses using an ammonia electrode. Phosphate was determined monthly and ammonia measurements were confirmed by laboratory analysis. The nutrient monitoring schedule and procedure was used indicate the need for nutrient applications. Unusually rainy weather experienced during several months of operation precluded accurate comparison of nutrient utilization and hydrocarbon biodegradation; therefore, nutrient utilization data are not shown. Soil pH was also monitored routinely; however, pH adjustments were not necessary during treatment.

EVALUATION OF PETROLEUM BIODEGRADATION

Treatment time for each cell ranged from five to eight months. Soil samples collected to confirm TPH treatment were analyzed using U.S. EPA Methods 418.1, 8015, 8015 modified for diesel, and ASTM Method D2887. Treatment cell 2/3 was the first to be samples for closure and its closure set a precedent for the other cells.

During the closure of treatment cell 2/3, several observations were made that impacted the interpretation of subsequent analyses. The observations involve potential interferences in Method 418.1, the TPH distribution in treated soil, and the type of TPH that remained in the soil after treatment. Consideration of these issues resulted in a much clearer understanding of the type of contamination, the risk associated with the remediated soil, and the performance of bioremediation.

Method 418.1 was conducted on randomly collected soil samples from treatment cell 2/3. Because of the complex nature of the contamination on site, the potential for method interferences was investigated. The standard operating procedure for Method 418.1 specified that silica gel treatments can be repeated until the TPH measurement does not change. Silica gel adsorbs nonhydrocarbon organic

compounds. Most laboratories perform only one silica gel clean-up. However, when two addition silica gel treatments were performed, the TPH concentration was reduced by about 300 mg/kg per sample. This represents a 15 to 20 percent decrease in TPH in most samples.

Results from Method 418.1 indicated that the TPH content of most soil samples was well below 1,000 mg/kg. However, a few samples were still very high and skewed the mean TPH to a value greater than 1,000 mg/kg in cells 2/3, 4, 5, and 6. Examination of the concentration distribution among the randomly collected samples from treatment cell 2/3 (Figure 2) indicated a nonparametric log-normal distribution. This type of distribution suggested that biodegradation affected the concentration of TPH within the soil since most samples were clustered toward low concentrations. High TPH concentrations were observed with a much lower frequency. The initial concentration of TPH had a normal (bell-shaped) distribution.

The mean and median of a normal distribution are points at which one half of the population is higher and one half is lower (7, 8). With log-normal distributions skewed toward the left or lower values, the median is the value at which one half of the population is lower and one half is higher. The mean of a log-normal distribution may be much greater than the median with much more than 50 percent of the samples falling below the mean. Therefore, the mean is not a valid indicator of the overall contaminant concentration in the soil when a log-normal contaminant distribution exists (7).

Observation of a log-normal TPH concentration distribution raised questions about the relatively rare high concentration samples. Further analysis of all samples from treatment cell 2/3 using U.S. EPA Method 8015, Method 8015 modified for diesel, and ASTM Method D2887 revealed that high molecular weight hydrocarbons similar to asphalt and coke residue contributed to the high TPH (>1,000 ppm) values observed in several samples. Table 2 summarizes the analytical results collected from 47 random samples collected from cell 2/3. Comparison of the median and mean values for TPH measured by Method 418.1 and diesel range TPH measured by modified Method 8015 indicated that approximately 50 percent of the TPH detected was not diesel or diesel range hydrocarbons. The absence of light weight hydrocarbons (gasoline and BTEX, data not shown) suggested that the extra material detected by Method 418.1 was high molecular weight hydrocarbons. Similarly, Figure 3 shows the sample concentration distribution observed when the same sample set was analyzed using Method 418.1 and Method 8015 modified for diesel. The TPH concentration range and the frequency of samples containing greater than 1,000 ppm TPH was greatly reduced in the Method 8015 results where high molecular weight hydrocarbons were excluded.

Application of ASTM Method D2887 to the samples indicated that a measurable and variable amount of the TPH was greater than C22, the hydrocarbon chain length recognized as high end for diesel range hydrocarbons by California standards. Even so, Method D2887 could not account for all of the TPH detected by Method 418.1.

Figure 4 compares the concentration of hydrocarbon fractions in representative samples before and after treatment. The results indicate that all hydrocarbon fractions were subject to treatment as indicated by the reduction observed in treated soil compared to untreated soil. While this was a very

encouraging observation, the total petroleum hydrocarbon content of the soil was still above the 1,000 mg/kg treatment level. Fractionation indicated that most of the residual hydrocarbon was much heavier than diesel components (greater than C22). In addition to reducing the overall TPH concentration, bioremediation treated lighter hydrocarbons to a lower level than heavier hydrocarbons.

The degree of hydrocarbon bioremediation is shown in Table 3. By comparing initial TPH values determined by Method 418.1 with final 418.1 values, percent reduction ranged from about 50 percent to nearly 90 percent. Accurate comparisons of initial and final diesel range hydrocarbons can not be determined because initial site characterization was conducted using only Method 418.1. An approximation of the percent reduction in diesel range hydrocarbons was calculated in Table 3. The values shown for the various analytical methods were determined by simply comparing the initial Method 418.1 results with the other methods. An alternative calculation was also conducted by subtracting the difference between the final Method 418.1 results and the other final results from the starting 418.1 values to give an initial value minus the high molecular component. Calculation of percent reduction using the modified starting values are shown in parentheses in Table 3. In summary, bioremediation resulted in greater than 80 percent reduction in hydrocarbon concentration in most cases.

Treatment time to achieve remediation ranged from five to eight months. Soil resided in some cells longer than 8 months because excessive rain hampered effective treatment as indicated by periodic monitoring (data not shown). Table 4 shows some the major cost elements for the project. The total cost to remediate the site was $55 per cubic yard. Costs directly associated with bioremediation activities totaled $27 per cubic yard.

CONCLUSION

Statistical evaluation of contaminant distribution and three different analytical methods were used to resolve the chemical nature of the residual contamination present in the soil following biological treatment. Following extensive discussions, this approach was considered by the involved regulatory agencies to be an unusual but accurate approach to evaluate the remediation process and demonstrate satisfactory site remediation. The result was cost effective closure of the site with permission to use the soil as clean fill material on site without restriction. Closure was granted based on the demonstrated nature of the residual contamination, the lack of health hazard associated with the high molecular weight, asphalt-like hydrocarbons, and the very low potential for off-site migration of hydrocarbons.

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Table 1
Bioassessment results

Parameter	Range
Heterotrophic Bacteria	2 x 10^4 to 1 x 10^7 colony forming units/g
Hydrocarbon-degrading Bacteria	5 x 10^3 to 3 x 10^6 colony forming units/g
Ammoniacal Nitrogen	61 to 237 mg/kg
Ortho-phosphate	6 to 1,280 mg/kg
pH	7.4 to 8.5
Soil Moisture	<1 to 14 percent

Table 2
Mean and median TPH concentration in treatment cell 2/3

Treatment Cell	Method 418.1 Mean (mg/kg)	Method 418.1 Median (mg/kg)	Method 8015 Modified Mean (mg/kg)	Method 8015 Modified Median (mg/kg)
1	791	380	380	145
2/3	1734	999	714	442
4	1225	830	553	455
5	1145	830	525	250
6	1489	1300	527	480

Table 3
Treatment effectiveness for TPH in soil

Cell	Initial 418.1 (mg/kg)	Final 418.1 (mg/kg)	Final 418.1 Reduction	Final 8015 (mg/kg)	Final 8015 Reduction	Final D2887 (mg/kg)	Final D2887 Reduction	Final TPH<=C31 (mg/kg)	Final TPH<=C31 Reduction
1	7,313	791	89%[1]	380	95% (94%)	478	93% (93%)	453	94% (94%)
2/3	3,201	1,734	46%	714	78% (67%)	1,294	60% (53%)	763	76% (66%)
4	11,250	1,225	89%	553	95% (95%)	726	94% (93%)	702	94% (93%)
5	4,142	1,145	72%	525	87% (85%)	647	84% (82%)	623	85% (83%)
6	3,865	1,489	61%	527	86% (82%)	696	82% (77%)	665	83% (78%)

[1] Values in parentheses represent percent removal corrected for recalcitrant TPH.

Table 4
Cost elements and cost per cubic yard

Analyze soil and assess site
Prepare plans,acquire permits, and submit reports
Screen Soil
Remove 13,000 cubic yards of debris for recycling
Scrape top 6 inches of soil from about 10 acres for treatment
Construct treatment cells with plastic covered berms
Place soil
Till each cell weekly for up to 8 months
Fertilizer
Monitor monthly
Manage rainwater for 3 months
Irrigate and control dust
Conduct closure sampling
Prepare reports and gain site closure
Remove soil from treatment cells
Remove berms and dispose of nonhazardous berm liners
$55 average cost per cubic yard (assumes 50,000 cubic yards of soil/debris handled during remediation). $27 average cost per cubic yard for activities directly related to bioremediation.

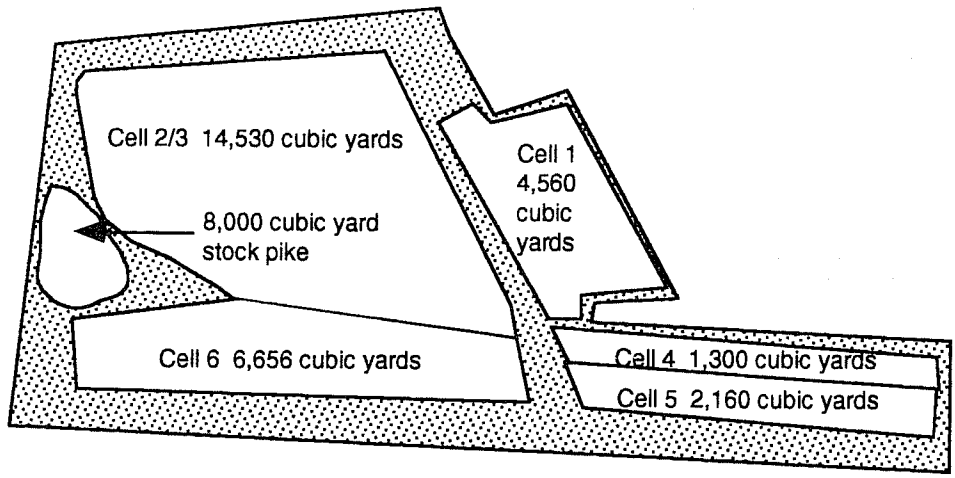

Figure 1. Site Map

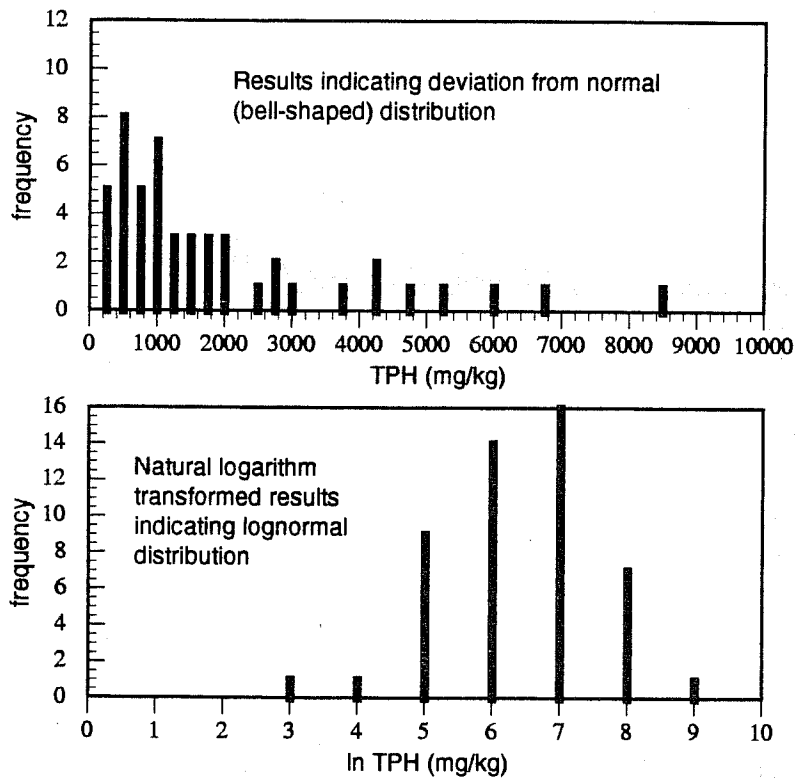

Figure 2. Demonstration of lognormal distribution of 418.1 TPH results.

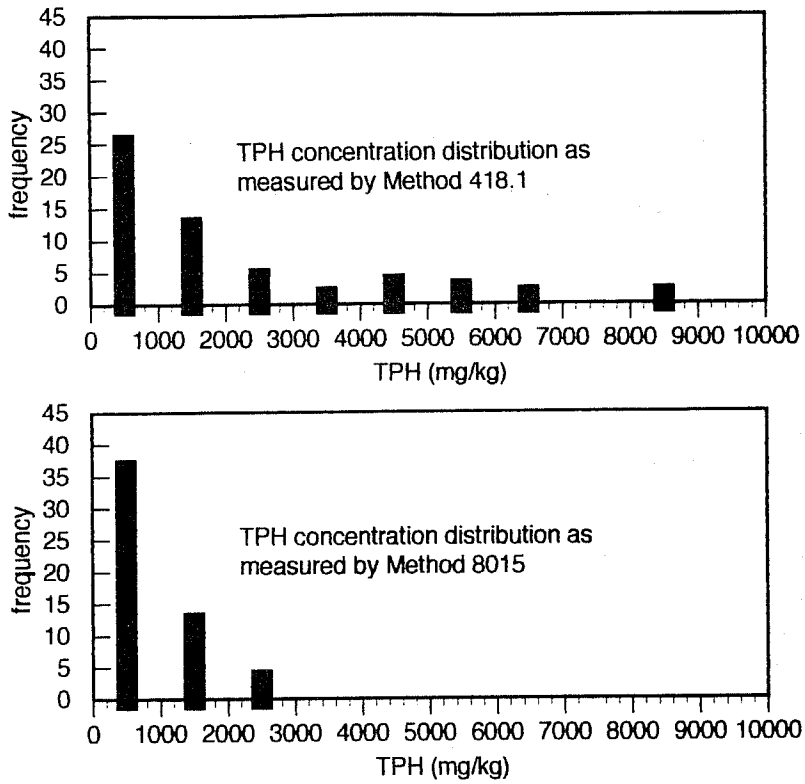

Figure 3. Distribution frequencies for TPH concentration in treatment cell 2/3 obtained by Methods 418.1 and 8015 modified for diesel.

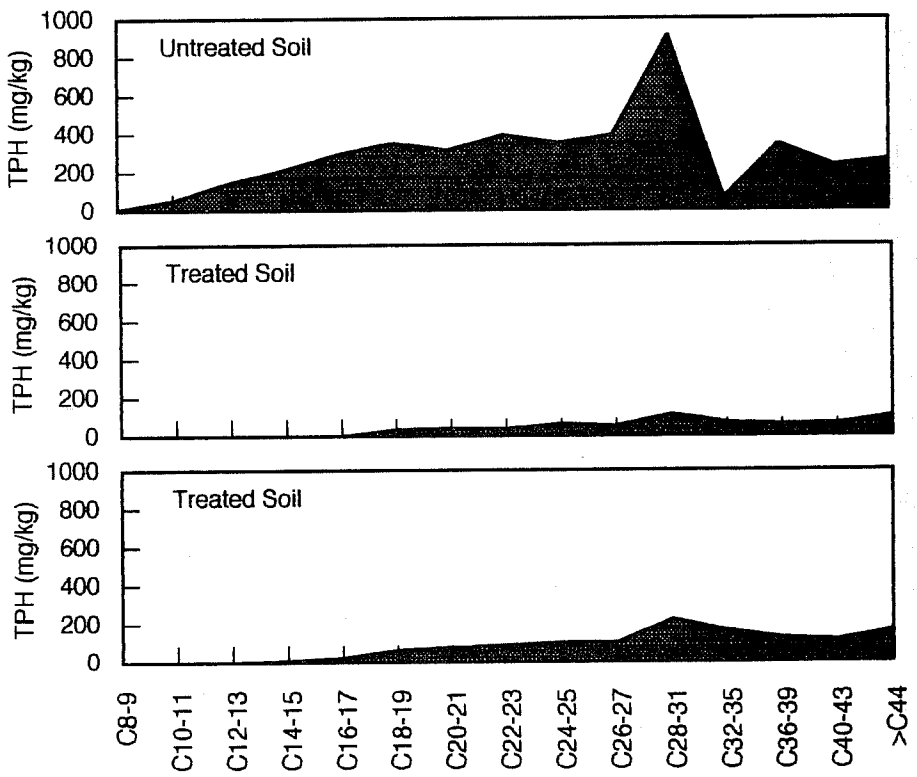

Figure 4. Comparison of hydrocarbon fraction concentration in soil before and after treatment.

Composting for Bioremediation of Oil Contaminated Soil

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A windrow composting process was used that exploits indigenous aerobic bacteria for the degradation of hydrocarbons. Lubricating oil-contaminated soils were excavated and amended with nutrients and bulking agents, then placed in rows three feet deep and about eight to ten feet wide on an impermeable surface. At this site, an unused building provided a treatment area with an enclosed and covered concrete floor. Plastic liner material was laid over the floor to contain any leachate from the soil piles. A bulking agent of wheat straw was mixed into the soil in an approximate ratio of 1 part straw to 4 parts soil by volume. Moisture in the compost mixture was maintained at about 50 - 60% of soil field capacity. Nutrient additions to achieve a C:N:P ratio of about 100:10:2 were calculated from an assumed stoichiometry at the initiation of each batch treatment in the windrows. Nitrogen was added as ammonium nitrate, which would also provide an alternate electron acceptor during low oxygen conditions. Compost piles were aerated by physically turning with a backhoe once every 7 to 10 days. Additional water was provided manually at this time from a well source on site.

Three 100 cubic yard batches of oil contaminated soils have been treated with this approach. The initial petroleum hydrocarbon (TPH) levels of up to 10,000 PPM were reduced to less than 50 PPM within three months. Reduction in hydrocarbon concentration was due to bioconversion because the relatively heavy lubricating oils were not subject to volatilization. Bacterial identification indicated six strains of known hydrocarbon degrading bacteria existing in the soil. Further testing revealed three that would consume hydrocarbons preferentially to other substrates. Rates of oil degradation were determined and correlated with nutrient availability, moisture, and bacterial counts in an effort to analyze the successful application of composting techniques to bioremediation of this soil, as well as to document the methodology which may be applied to other similar sites.

STATEMENT OF PROBLEM

The nature of operations in the oil and gas industries continually generates soils contaminated with hydrocarbons in the form of crude, lubricating oils, transmission fluids, hydraulic fluids, natural gas condensate, gasoline and other refined volatiles. Historically, the source of this contamination is from leaks or spills at transfer connections at tank batteries, production facilities, compressor engines, underground storage tanks, machinery/equipment storage areas, maintenance centers and as a result of pipeline leaks or ruptures. In the past these soils were excavated and spread on roads for dust control, left in place and covered with clean soil or gravel, or landfilled. The Resource Conservation and Recovery Act (RCRA), Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, i.e. Superfund) and the Clean Water Act now require remediation of these soils and have also severely restricted disposal options. The industry is discovering that an economical and practical method of remediating these large quantities of oil contaminated soils is through bioremediation processes.

The aim of this study is to demonstrate bioremediation of soil contaminated with lubricating oil from around compressor engines on natural gas pipelines. Almost all these engines leak lubricating oil at various connections, seals, and gaskets. Some companies commonly install engines on concrete foundations without any gutters, troughs, rails or other measures to collect oil along with any contaminated storm or engine wash-down water. The oil and contaminated water runs off the foundation into the surrounding soils. Typically, depending on the type of engine and length of service, the contaminated soils extend to a depth of 18 to 24 inches and 4 to 5 feet around the perimeter of the foundation. With an average size foundation being 8 feet by 20 feet this results in approximately 16 cubic yards of contaminated soils at each engine. Thousands of these engines operate on various pipelines, processing plants, and refineries in Oklahoma.

PROJECT OBJECTIVES

The objectives of the experiments conducted during this project were to determine:

1) if soils contaminated with lubricating oil and other long-chain hydrocarbons could be effectively remediated through windrow composting systems, on a full-scale basis using only indigenous bacteria;
2) the environmental and operating conditions, and the types and populations of bacteria, that promoted effective degradation of these hydrocarbons.

Most of the studies conducted to date on this type of contaminant have involved laboratory beaker, bench-scale or pilot-scale testing. This project involved a full-scale, ongoing remediation project of soils contaminated with lubricating oil under field conditions. No inoculum preparations of exogenous or indigenous bacteria were used. These experiments provided substantive data on the effects of manipulating environmental conditions (moisture, nutrients, oxygen, soil porosity, etc.) to enhance hydrocarbon degradation rates by indiginous bacteria. The experiments included specific analyses on the types of bacteria which were the most aggressive hydrocarbon degraders present, response of the bacteria to changes in environmental conditions, and changes in population levels over the duration of the project.

ENVIRONMENTAL FACTORS

An attempt was made to initiate and maintain a high level of microbial activity in the soil composting experiments by optimizing various environmental factors which have been shown to affect degradation rates. These factors include mineral nutrients for bacterial growth, moisture, temperature, oxygen availability, and soil composition.

NUTRIENTS

Microbial metabolism and growth is dependent on adequate supplies and proper ratios of nitrogen, phosphorus and other micro-nutrients or trace elements (i.e. sodium, potassium, calcium, magnesium, iron, etc.). During bioremediation processes (e.g. composting), microorganisms consume carbon for growth and also especially nitrogen for protein synthesis. Common C:N ratios used for oily sludges and waste oils in soils have ranged between 10:1 and 25:1 (1,2). The sole carbon source in most inorganic predominant soils will be the hydrocarbon contaminant or the total petroleum hydrocarbon level. If an inadequate supply of nitrogen exists, then the organisms' growth rate will be retarded. If nitrogen levels are too high, then excess nitrogen will be lost as ammonia. At high enough levels, ammonia can retard the breakdown process (3). Phosphorus to nitrogen ratios of approximately 0.2 have proven effective in this study and others (2). Overall, the microbial requirements for nutrients are approximately the same as the composition of the cells. One additional consideration is to add nitrogen in the form of ammonium nitrate. Nitrate can be utilized as an additional electron acceptor by facultative anaerobes if oxygen supplies are decreased (4).

MOISTURE

The optimum moisture content for aerobic remediation in this study and others cited has been 50 to 60 percent of field capacity, or approximately 6 - 8 percent by weight of inorganic based soils. However, field capacity will no longer be applicable when soils are excavated and bulking agents are added, as in this composting study. The percent by weight basis or physical observation should be used to ensure that soils are moist but do not form slurries with free drainage of water.

The greatest diversity and activity of microorganisms and the highest population densities are consistently observed in the sandy water-bearing strata, whereas the dense, dry-clay layer zones have the least microbial activity (4). Too much moisture can result in toxic anaerobic conditions developing, and too little has been found to severely limit degradation rates (5). Generally, with decreasing water potentials, fewer organisms are able to grow and reproduce. When soils become too dry, many microorganisms form spores, cysts, or other resistant forms, whereas many others are desiccated (6).

TEMPERATURE

Although biodegradation occurs at a temperature of 5°C, hydrocarbons degrade much more slowly at these lower temperatures. Most soil microorganisms

are mesophiles and exhibit maximum growth in the range of 20 to 35°C (3). The majority of hydrocarbon utilizing bacteria are most active in this range (4).

OXYGEN

The biodegradation of most organic contaminants requires approximately two parts oxygen to completely metabolize one part of organic compound (6). The complete oxidation of 1 mg of hydrocarbon to carbon dioxide and water requires 3 to 4 mg of oxygen (4). The optimum level for aerobic metabolism is greater than 0.2 mg/l of dissolved oxygen and a minimum air-filled pore space in the soils of 10% (4). These oxygen levels can be maintained in passive bioremediation type processes (e.g. windrow composting, landfarming, shallow in-situ) by prevention of saturation with water, presence of sandy and loamy soils and a bulking agent (e.g. wood chips), moderate tilling, avoidance of compaction of soil, and limited additional carbonaceous materials.

SOIL COMPOSITION

Soil composition influences infiltration rate, permeability, oxygen diffusion, water holding capacity, and adsorption capacity for various waste components. The predominance of clay and silt particles in finer textured soils results in a very small pore size with a slow infiltration rate of water (low porosity) and a low diffusion rate of oxygen. Clay soils tend to retain a higher moisture content which can further restrict oxygen diffusion. Coarse soils of sand and gravel with large interconnecting pores allow sufficient oxygen diffusion and rapid water movement. However, if the soils are excessively drained, added nutrients may be lost.

A bulking agent addition has been found critical for successful remediation of hydrocarbon contaminated soils in prepared bed and composting remediation processes regardless of soil types but especially for cohesive clay-based soils. The bulking agent increases or maintains porosity of the soil for adequate distribution of nutrients and diffusion of oxygen, heat, and waste gases. These agents have included wood chips, straw, and sawdust. A typical soil to bulking agent ratio (per volume) is 4:1 with an overall porosity of approximately 40 percent (7,8). Typically, a trial and error method will be needed to find a ratio for specific soil types to maintain proper oxygen, moisture and porosity rates.

MICROBIAL POPULATIONS

The microbial community in soil usually includes a significant hydrocarbon utilizing component, which readily increases in response to hydrocarbon contamination. These indigenous microbial populations are also highly adapted to a particular soil environment. Exogenous or seeded microorganisms generally cannot compete successfully and survive; for this reason, soils are not widely considered to be amenable to improvements in rates of biodegradation through seeding alone (9). Other potential problems associated with the inoculation or seeding of soils with exogenous organisms include: the presence of inhibitory substances, predation, preferential metabolism of competing organic substrates, and insufficient movement of the seed organisms within the soil.

EXPERIMENTS

CONTAMINATED SOIL

Soil contaminated by lubricating oil was excavated from around natural gas pipeline compressor engines for treatment. These soils may have also been contaminated with ethylene glycol which was used as a coolant and were analyzed for hazardous constituents under RCRA toxic characteristic leachate procedure (TCLP). These tests included analysis for heavy metals, volatiles and semivolatiles. The results indicated that all of these constituents were present at less than the detection limits except for barium of 0.14 mg/kg. The pH was not tested but based on the known nature of the contaminant and inorganic content of the soil, it was presumed close to neutral. All of the batches were tested throughout the experiment for total petroleum hydrocarbons (TPH) as the indicator parameter for the contaminant. All of the soils were excavated from around compressor engines in a common area; all had been exposed to the same type of lubricating oils. The target remediation level was 50 mg/kg TPH.

TREATMENT METHODOLOGY

Three batches of soil were treated from May 1992 through November 1993. The first batch comprised 133 cubic yards of soil, the second 89 cubic yards and the third 75 cubic yards of soil. These soils were treated in an abandoned warehouse on the plant site under ambient temperature conditions. A bench scale test was conducted simultaneously on the first batch and was used to confirm residual TPH levels and nutrient requirements. A bench scale test was also conducted simultaneously with the third batch of soils to monitor biological activity. This bench scale test comprised two cells of approximately 0.5 cubic yards of soil each. One cell contained contaminated soils from the third batch and the other "control" cell had uncontaminated soils from the same plant area. The soils were mixed with a nitrogen fertilizer and bulking agent of wheat straw, and water was added from a well supply. The TPH, nutrient and moisture levels were sampled and analyzed approximately every 14 - 18 days. The warehouse was covered, had a concrete floor, and was large enough to accommodate the largest batch at a windrow depth of three feet. The bench cells were turned by hand and sampled and watered on approximately the same frequency as the field test compost piles.

COMPOSTING PROCESS

Bulking agent was mixed with the soils in an approximate ratio of 1 part wheat straw to 4 parts soil. Ammonium nitrate and ammonium phosphate, obtained at the local farmer's cooperative at a cost of less than $10 per 50 pound bag, were added to establish an initial C:N:P ratio of 100:10:2. This was accomplished by nitrogen and phosphorous analysis and calculating deficiencies based on the volume of soil and level of contamination. The first batch treated had the greatest nutrient deficiencies which corresponded to the higher levels of TPH contamination in this batch. Because the soils were primarily inorganic (sands and gravel), the total petroleum hydrocarbon (TPH) levels were used as the basis for the total organic carbon content in the soil. Water was added to the soils from a well supply to keep the soils saturated to a point that no free liquids, drainage or slurries

were produced. Water was added when the soils were turned to allow proper mixing and consistency. It was estimated that the moisture content of the soils was approximately 40 to 50% of a theoretical field capacity based on observations and moisture weight percent. The soils from all three successive batches were spread out into two piles (or rows) in the warehouse. The piles were 40 feet by 10 feet by 2 to 3 feet deep. A 10 foot center aisle was left open for access. The windrows were turned every 7 to 10 days with a backhoe for aeration. Water and nutrients were also added at this time if needed. Samples were usually also collected at this time for analysis. Periodic maintenance required approximately two labor hours to complete.

SAMPLING AND ANALYSIS

Sampling and analysis were performed for TPH, moisture, volatile solids, ammonia nitrogen, nitrate nitrogen, and phosphate. The bench test associated with the third batch was analyzed initially for total heterotrophic plate count, bacterial identification and endpoint assay; subsequent samples were taken for plate counts only. These plate counts were correlated to the initial identification to determine the population of the hydrocarbon degrading species. Composite samples were taken which consisted of soils from at least four random areas and depths in the warehouse (field) and bench studies.

For the first batch, TPH was sampled at the start of the treatment process and was not sampled again until five months later. At this time it was discovered that detectable TPH levels were not present. Samples were not taken more frequently because of difficulties in setting up the project, establishing procedures, and assigning manpower responsibilities for sampling. Samples were obtained and analyzed approximately every 14 days for the second batch and approximately every 14 days for the bench study of the third batch. TPH samples were analyzed about once every 30 days for third "field" batch. One TPH analysis was performed on the uncontaminated "control" bench cell.

Samples and analysis for moisture, nutrients, and volatile solids were taken approximately every 30 days for the first and third batches and every 14 to 30 days for the second batch. For the third batch, samples were only taken from the field project and correlated to the bench test. Volatile solids results were inconclusive and did not correlate to increases in cell mass or other factors. As such, they were not reported nor used as an indicator parameter. In addition, moisture requirements of the soil were assessed only by physical observation in an effort to maintain the soils at optimum moisture conditions.

TPH ANALYSIS

TPH was analyzed by a commercial laboratory using EPA Method 8015, a gas chromatography analysis with methane or hexane extraction to chart hydrocarbon signatures or spikes by molecular weight. The non-volatile 8015 method which will detect hydrocarbons from C_{10} to C_{50}, including the lubricating oil contaminant in these soils, was specified for these tests. Any volatile hydrocarbons less than C_{10}, which existed in the soil or were a result of biodegradation of the longer-chain hydrocarbons, were not monitored because they typically would be volatilized during aeration of the soils.

MOISTURE/NUTRIENT ANALYSES

Moisture of the soil was determined according to Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 209A. Volatile solids were determined according to Method 209G, ammonia nitrogen according to Method 417C which includes nitrogen in the sorbed and aqueous phases, and phosphate phosphorus and nitrate nitrogen according to Method 429.

SOIL TYPE

A sieve and mechanical analysis of a composite sample representative of the soils from the three batches treated was performed. The soils were comprised of 42% gravel, 50.4% sand, and 7.6% clay or silt by weight. The high gravel content is not unusual because of successive layers of gravel used over the years around the engines as a ground cover. The high sand percentage was also expected because the engines were located in the Cimarron River valley.

BIOLOGICAL ACTIVITY

During the testing of the third batch of soils, samples were taken from parallel bench-scale units and shipped to a commercial laboratory for analysis of biological activity. Analysis consisted of total plate count, bacterial identification, and an endpoint assay. Subsequent samples were cultured for total plate counts and compared to the initial identification analysis to determine the specific counts of bacteria types within the population.

Standard Bacterial Plate Count

A standard spread plate method was used for this process. Aliquots from each sample were checked for weight and then serially diluted. Each dilution was then transferred in a sterile form to a laminar flow biological cabinet and placed on a previously prepared and dried trypticase soy broth agar (TSBA) medium in Petri plates. Observations for colony forming units (CFU) were made at 24 and 48 hours on incubation at 28°C for each sample. The different types of bacterial colonies formed were noted after 48 hours of incubation. These were counted and compared by one of two specific bacterial identification procedures.

Bacterial Identification

Two different analysis methods were used to identify the bacterial strains, the Gas Chromatography Fatty Acid Methyl Ester (GC-FAME) System and the Biolog Microplate System. The GC-FAME method identifies bacteria based on unique fatty acid profiles. These profiles are identified by gas chromatography and are compared to a database consisting of more than 60,000 profiles of strains. The Biolog Microplate method characterizes bacteria by carbon source utilization tests. There are 95 wells on a microplate which contains a carbon source and a tetrazolium dye. As the bacteria consume the carbon source in a well, the dye turns purple. Each species of bacteria creates a distinct pattern of purple dots that is recognized by the automated microplate reader and compared to the Biolog database. The species characteristics in the GC-FAME and Biolog databases are an "average" of the characteristics of hundreds of tested bacteria of the same species. The similarity and distance coefficients of the organism are calculated based on a

hypothetical 'mean' organism in the databases. The database organism has a similarity coefficient of one and a distance of zero. The closer the test strain is to one and zero the more closely it matches the mean organism in the database.

Endpoint Assay

The endpoint - kinetic assay measures the effectiveness of specific bacteria found in soil or water to break down hydrocarbon contaminants. After the plate counts, specific bacteria strains were isolated and grown for 18 hours on TSBA. The bacteria were then separately loaded into 96-well microtiter plates in which an undisclosed growth medium (mineral salts, vitamin mix , buffer) was added without a major carbon source. The wells also contained a tetrazolium dye which was activated by the microbial oxidation of the carbon source. Free phase contaminant from the site was then added to selected wells. The bacterial strains were then allowed to grow and consume the contaminant as their carbon source. Based on the initial identification, counts were then made of each specific strain type. TSBA without contaminant served as a positive growth control. The bacterial strains were also cultured on the oil and the TSBA separately as their sole carbon sources. The purpose was to determine their preferential substrate source and growth rates on each per strain. Bacterial growth was measured by color intensity of the dye after 24 hours of incubation.

RESULTS

The results of the analyses performed for the compost treatment of batches one through three and the bench study concurrent with batch 3 are identified below with reference to appropriate tables and figures.

Batch One

Table 1 summarizes the treatment results from batch one (the first full-scale composting field trial). Three separate composite samples were taken for the nutrient and other parameters and one composite sample for TPH. TPH levels were only identified at the beginning and end of the treatment process.

The lubricating oil in the contaminated soil in this batch was successfully remediated to non-detectable levels within a period of six months. The total nitrogen levels (ammonium and nitrate) reflected an increase in microbial activity with a significant consumption of nitrogen during this process. The total nitrogen levels taken on 17 September were 1,857 mg/kg and approximately 30 days later were 486 mg/kg. It can be assumed that the nitrogen addition made between July and September of that year was a critical factor for the success of this treatment.

Batch Two

Table 2 summarizes the treatment results from batch two. Four separate composite samples were taken for nutrient and other parameters and one composite sample for TPH.

The lubricating oil in the contaminated soil was successfully remediated below the target level of 50 mg/kg during the three month treatment process. Nitrogen consumption corresponded with the hydrocarbon degradation rates as

evidenced by total nitrogen levels of 678 mg/kg on 21 April and 226 mg/kg on 13 May. Following this analysis, nitrogen was added at the end of May, bringing the level to 1,380 mg/kg in June. Correlation between nitrogen uptake and the decrease in TPH levels between March and May is clearly evident. Figure 1 tracks the concentrations of TPH, nitrogen and phosphorus over the treatment period.

Batch Three

Table 3 summarizes the treatment results from batch three. Two separate composite samples for nutrients and other parameters and one composite sample for TPH were taken from the field composting location.

The lubricating oil contaminant was degraded from initial levels of 1,601 mg/kg to 175 mg/kg. The duration of the treatment process was three months. The target level of 50 mg/kg was not reached during this time because of the onset of cooler weather and the probable resulting decrease in microbial metabolic activity. The treatment and monitoring of this batch will continue in the spring of 1994. Figure 2 shows the changes in TPH, nitrogen, and phosphorus levels.

The nitrogen and phosphorus levels decreased dramatically from 1,017 mg/kg and 2,743 mg/kg respectively in July to 93 mg/kg and 366 mg/kg in August. Although this may be due in part to sampling anomalies, nitrogen uptake should and did correlate to changes in TPH levels and increases in microbial activity.

Batch Three (Biological Data from Bench-Scale Tests)

The soils from the two bench test cells were sampled for biological activity and TPH levels. One cell contained soil from batch three of the field test, and the other contained uncontaminated soil from the same general plant area. Both cells were treated with water and aerated identically. Nutrients were also added to both cells based on deficiencies identified from the soils in the field test. Initial total plate counts identified substantial populations (7.81×10^8 colony forming units per gram (CFU/g) in the cell with contaminated soil) of hydrocarbon degrading bacteria in both cells, representing six strains identified in Table 4. Species identification was accomplished by comparing the results of the GC-FAME and Biolog methods. A good match to the database organism is considered one with a similarity coefficient greater than 0.5 and a distance coefficient of less than 7.0.

Endpoint assay testing concluded that strains #1, #3, and #6 were the most aggressive hydrocarbon degraders. Figures 3 and 4 illustrate that these strains consumed oil as their carbon source almost as readily as the TSBA medium and that their growth was greater than the other three strains on the oil substrate.

During the batch treatment experiments, strains #1, #3, and #6 dominated the population with 88% of the total count during the first month of treatment and with total plate counts increasing during this time. At the beginning of the second month, strains #2 and #4 then began to dominate with 70% of the total population with only moderate increases in total growth. At the end of the second month strain #6 and previously unidentified strains accounted for 75% of a decreasing total population. Figure 5 identifies the composition of the various strains in proportion to the total population, while Figure 6 shows the total count per strain over the treatment period. Increases in total population counts correlated with decreasing TPH levels. There was also a noticeable shift in strain domination and composition over the treatment period. This can be expected because of the substrate changes

due to the degradation of this complex mixture of longer chain hydrocarbons to simpler products preferred by other microbes. Control soil units contained much lower microbial numbers, which also dropped over time.

CONCLUSIONS

This testing has demonstrated that inorganic based soils contaminated with lubricating oils up to 10,000 mg/kg can be remediated to less than 50 mg/kg within three to four months. Although the TPH level in batch three was 175 mg/kg at the end of this test, it is expected, as evidenced by testing of the other two batches, that further treatment during warmer months will further reduce these levels to below 50 mg/kg. The treatment period for batch one was six months. However, the TPH levels were not monitored closely during this time and it is anticipated that the target level would have been reached in half the time if the nutrient and moisture additions and sampling regime had commenced earlier, based on the subsequent results.

Other studies have shown that this same type of treatment process should also be effective for other heavier, long-chain hydrocarbon contaminants in different types of soils (5,10). The results also indicate the oil contaminant was removed by biological degradation and not by other processes, such as volatilization or solubilization and dispersion in the treatment water. Long-chain hydrocarbons such as these are not subject to volatilization even during mechanical aeration of soils because of their heavy formula weights and high boiling points. This is also evidenced by the fact that surface spills of these hydrocarbons are prevalent for many years even after constant exposure to sunlight, heat and oxygen. There was no evidence of leachate formation. Endpoint assay and plate count tests confirmed the presence and growth of hydrocarbon degrading bacteria, providing positive evidence of bioremediation.

A bulking agent of wheat straw proved very effective with the sandy, gravelly soil tested in this study. If more cohesive soils such as clay or organic based soils are treated, other materials may be more effective. The straw did not decompose significantly over the six month treatment process and was an important conduit for moisture and oxygen transfer. This was especially critical since the soils were not turned or watered except every 7 to 10 days. The addition of moisture based on physical observation proved effective by avoiding any free drainage or slurrying. The moisture level should be close to the reported optimum of 50 percent of field capacity based on observations from other studies.

Based on this study, the cost of this windrow composting approach, assuming similar conditions, 100 cubic yard batches of soil, and minimal monitoring for TPH, nutrients and biological activity, would be approximately $15 per cubic yard. This compares to approximately $30 for forced air static-pile compost processes, $50 to $100 for special industrial waste landfills and enclosed bioreactor methods and $1,000 per cubic yard for hazardous waste landfills.

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Table 1

Summary of Results from Batch One

Volume of Soil:	133 cubic yards
Initial TPH Level:	9659 mg/kg (PPM)
Ending TPH Level:	< 1 mg/kg (field)
Duration of Treatment:	6 months (5/92 - 11/92)
Nutrient Additions:	700 lbs. ammonium nitrate 350 lbs. ammonium phosphate
Estimated Cost:	$1,700 ($800 labor, $400 material, $500 analysis)

Table 2

Summary of Results from Batch Two

Volume of Soil:	90 cubic yards
Initial TPH Level:	3006 mg/kg
Ending TPH Level:	48 mg/kg
Duration of Treatment:	3 months (3/93 - 6/93)
Nutrient Additions:	200 lbs. ammonium nitrate 0 lbs. ammonium phosphate
Estimated Cost:	$1,600 ($800 labor, $100 material, $700 analysis)

Table 3

Summary of Results from Batch Three

Volume of Soil:	75 cubic yards
Initial TPH Level:	1601 mg/kg
Ending TPH Level:	175 mg/kg
Duration of Treatment:	3 months (8/93 - 10/93)
Nutrient Additions:	200 lbs. ammonium nitrate 0 lbs. ammonium phosphate
Estimated Cost (field):	$1,000 ($600 labor, $100 material, $300 analysis)
Estimated Cost (bench):	$1,500 ($200 TPH, $500 plate counts, $800 endpoint assay)

Table 4

Identification of bacterial strains

Summary of GC-FAME/Biolog Analyses							
Strain Name	**Primary Identification by GC**	**Sim. Coef.**	**Dist Coef.**	**Primary ID by Biolog™**	**Plate Type**	**Sim. Coef**	**Dist. Coef**
2337-1	*Escherichia coli*	0.268	5.246	*Klebsiella pneumonia A*	GN	0.668	5.015
2337-2	*no ID closest species Bacillus megaterium*	0.49	3.859	*no ID closest species Staphylococcus simulans*	GP	0.463	7.639
2337-3	*Enterobacter sakazakii*	0.252	5.365	*No ID closest species Citrobacter freundii*	GN	0.158	15.463
2337-4	*Gordona bronchialis*	0.522	3.685	*no ID closest species Rhodococcus erythropolis*	GP	0.182	15.883
2337-5	*Pseudomonas aeruginosa*	0.287	6.851	*Klebsiella pneumoniae A*	GN	0.866	2.153
2337-6	*Pseudomonas aeruginosa*	0.661	4.222	*Pseudomonas citronellolis*	GN	0.515	4.834

Strain #	**Closest Match**	**I.D. Method**
#1	*Klebsiella pneumonia*	Biolog
#2	*Bacillus megaterium*	GC-FAME
#3	*Enterobacter sakazakii*	GC-FAME
#4	*Gordona bronchialis*	GC-FAME
#5	*Klebsiella pneumoniae*	Biolog
#6	*Pseudomonas aeruginosa*	GC-FAME

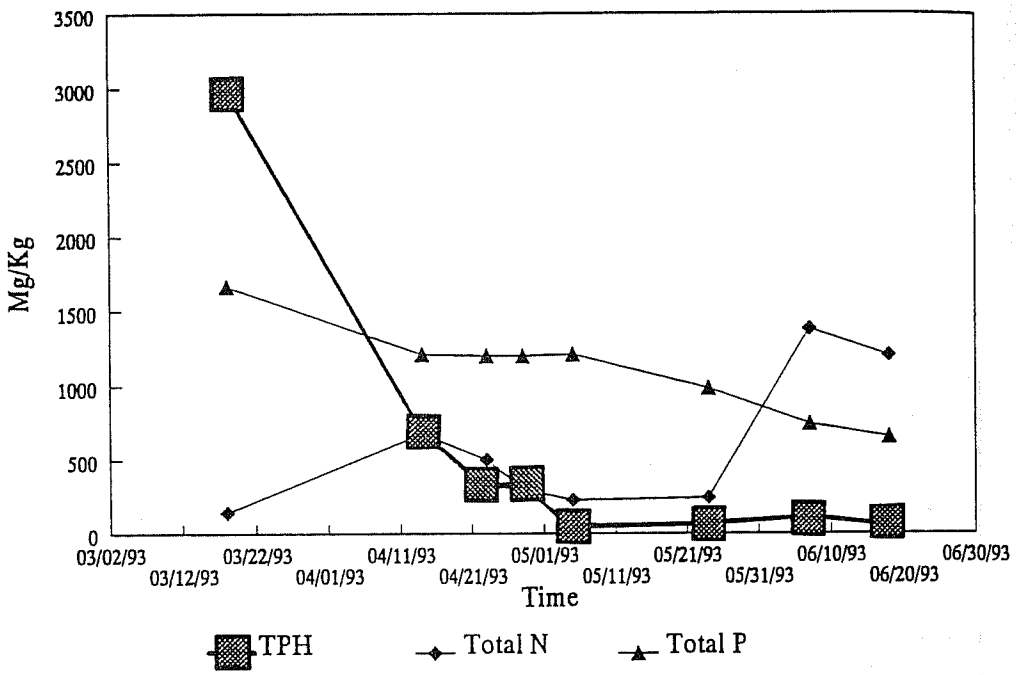

Figure 1. Batch Two TPH, nitrogen, and phosphorus levels.

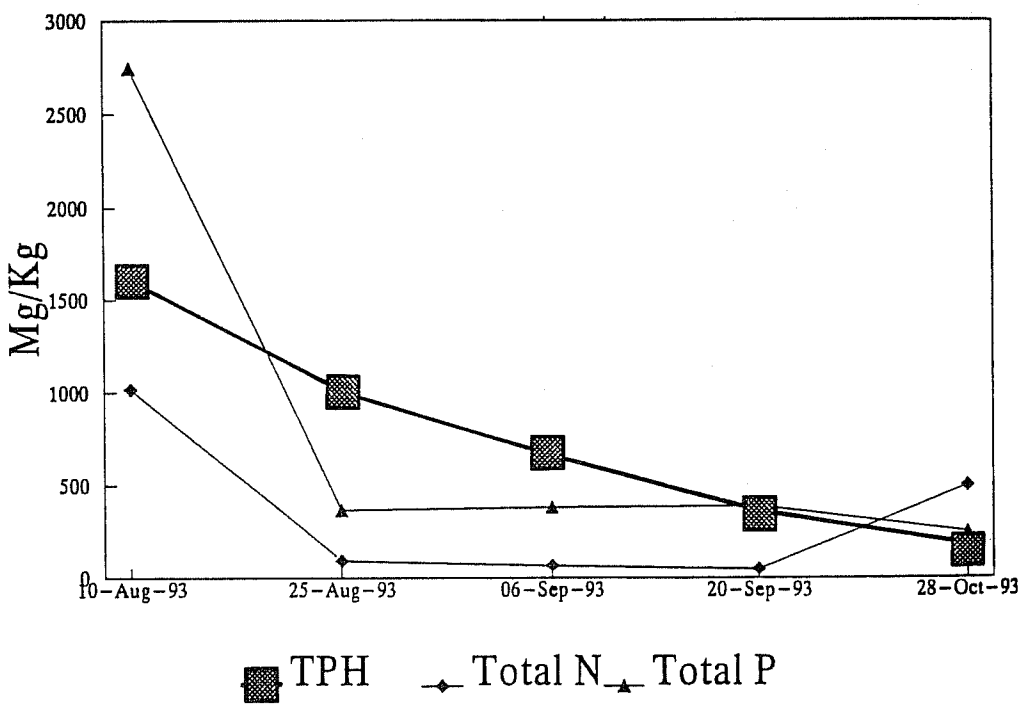

Figure 2. Batch Three TPH, nitrogen, and phosphorus levels.

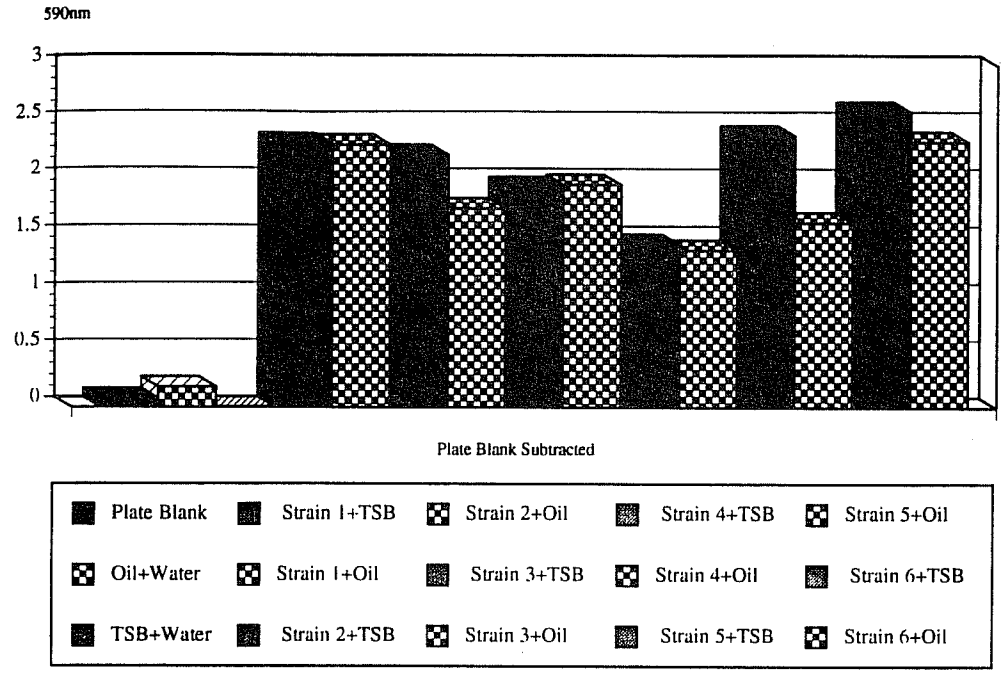

Figure 3. Growth of bacterial strains on TSBA medium and oil.

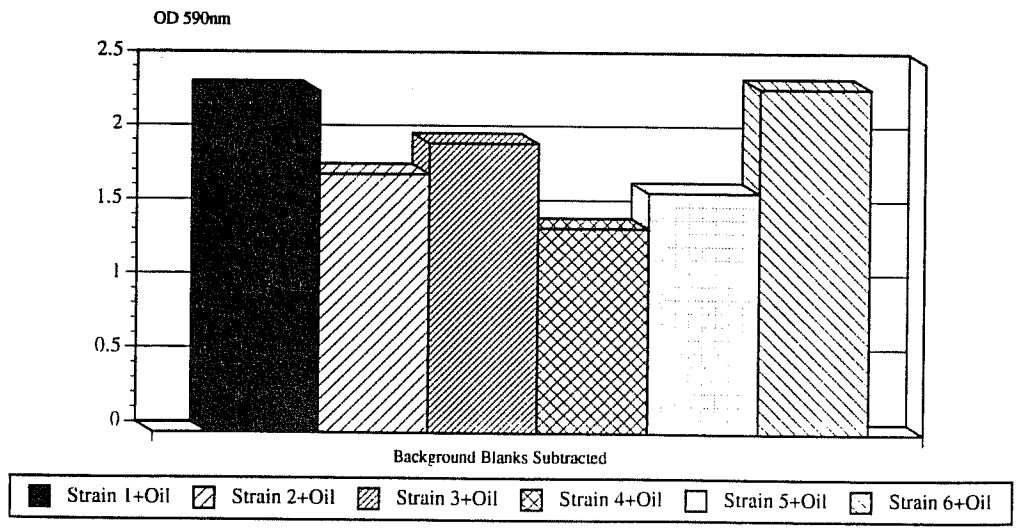

Figure 4. Growth of bacterial strains on oil only.

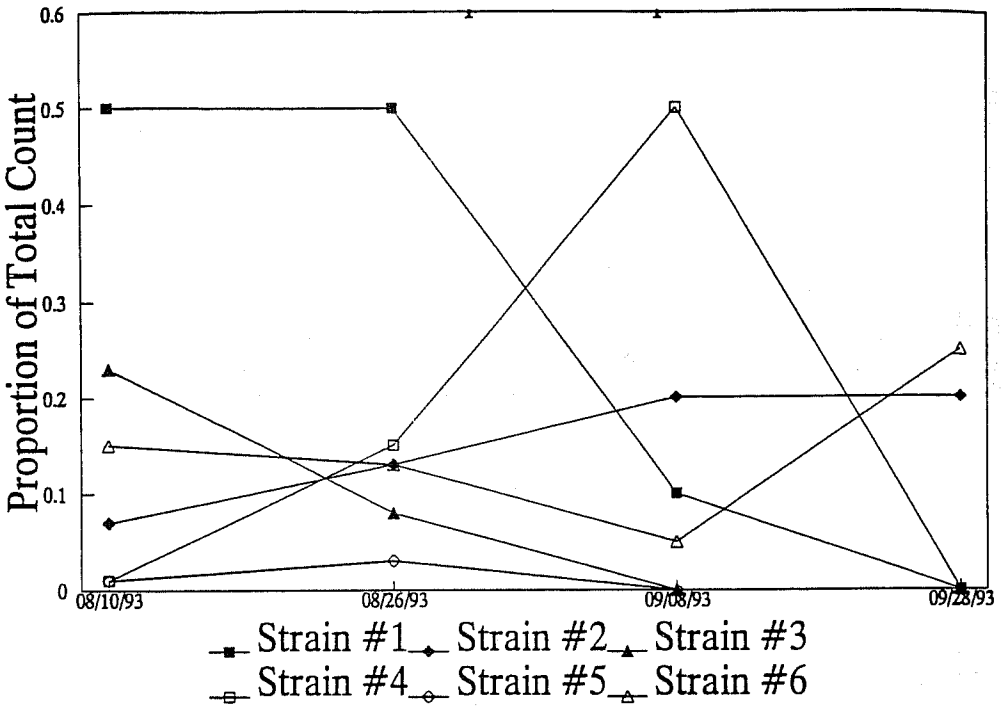

Figure 5. Proportion of strain growth to total bacterial population.

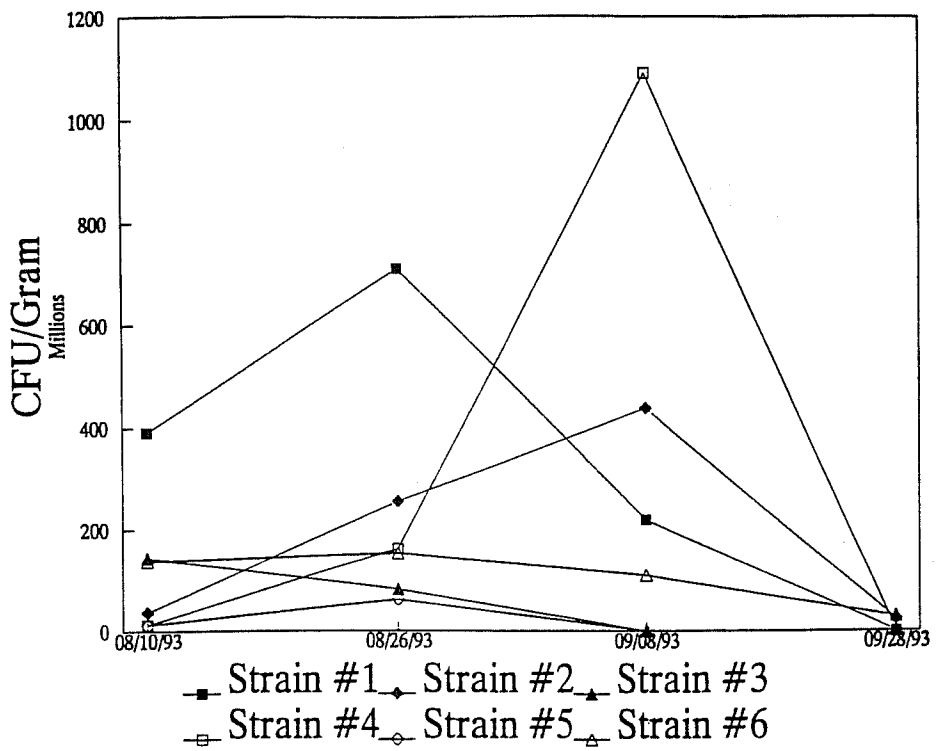

Figure 6. Total count per bacterial strain.

Microbial Transformations of Sulfur Compounds

Microbial Desulfurization of Petroleum: Fundamental Study on Dibenzothiophene Desulfurization by *Sulfolobus acidocaldarius*

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Abstract

The capability and characteristics of an extreme thermophile *Sulfolobus acidocaldarius* in degrading model organic sulfur compounds of petroleum oils were examined in this study. Sulfate release was observed when viable cells were inoculated in shaker's flasks containing basal mineral media with dibenzothiophene (DBT), phenyl sulfide and butyl sulfide. The cell concentrations continued to decrease, indicating the inability of these compounds in supporting cell growth in shaker's flasks. However, in further studies with a highly agitated fermentor, *S. acidocaldarius* was observed to grow in a media with DBT as the only possible source of organic carbon and sulfur with a doubling time of *ca.* 3.5 days, although the maximum cell concentration reached was extremely low, i.e. 42 mg DCW/L. When inoculated with more cells, the cell concentration was found to drop rapidly but stabilize at about the same steady level of 44 mg DCW/L. The low maximum supportable cell concentration was therefore attributed to the severe mass transfer limitation of DBT to cells, due to negligible solubility of DBT in the aqueous media. In another fermentor run where cells were grown in a DBT-containing medium supplemented with tryptone and yeast extract, both cell growth and DBT transformation were found to be much faster. The enzymes responsible for desulfurization were, therefore, not repressed by the presence of other organic substrates (tryptone/yeast extract). With GC/MS analysis, 2'-hydroxybiphenyl-2-sulfinic acid, phenoxathiin and 4-hydroxybenzoic acid were tentatively identified as metabolic intermediates of DBT degradation. It appears that *S. acidocaldarius* oxidizes the sulfur of DBT initially, cleaves the C-S bonds to release sulfate into the medium, and then further degrades the carbon structure of the intermediates.

INTRODUCTION

Crude oil is characterized by the presence of objectionable quantities of organic sulfur compounds. These can generally be classified into three types: sulfides, thiols and thiophenes. The increased costs of conventional methods of desulfurization, together with depletion of high-grade reserves and stricter environmental regulations, have stimulated consideration of alternative technologies, including biotechnology (1). Several reports discussed the biological oxidation of model organic sulfur compounds by various microorganisms (2,3). Generally regarded as a good model compound representative of organic sulfur found in petroleum and coal, dibenzothiophene (DBT) degradation has been most extensively studied. However, for potential commercial application, it is desirable for the microorganism to have wide desulfurization capabilities for removing other thiols, thiophenes and sulfides from the oil. Furthermore, the microorganism under consideration should selectively cleave the carbon-sulfur bond and leave the carbon structure of the organosulfur compound intact so that the release of organosulfur heteroatom is achieved without loss of fuel value.

In this study, the capability of *Sulfolobus acidocaldarius* to desulfurize DBT, phenyl sulfide (PS) and butyl sulfide (BS) were examined. *S. acidocaldarius* was chosen because: (a) the species is a thermoacidophilic archaebacterium thriving at low pH (less than 3.00) and high temperature (65-90^{0}C) thereby offering the benefits of reduced culture contamination as well as increased reaction (desulfurization) rates and (b) the reported sulfate release from dibenzothiophene by *S. acidocaldarius* indicates a possible sulfur-specific pathway (4).

There are several reports in the literature that discuss the capabilities of *S. acidocaldarius* in organic sulfur oxidation (4-9). Unfortunately certain conflicts also exist. Kargi and Robinson claimed that *S. acidocaldarius* grew as a heterotroph at the expense of DBT, although growth was not quantified but reported as "slight increase in cell concentration on microscopic observation". Krewiec and Montenecourt (9), on the other hand, reported the inability of *S. acidocaldarius* to grow on DBT as a sole source of organic carbon or sulfur. In addition, noxious effects of DBT on heterotrophic growth of *S. acidocaldarius* with another organic substrate (yeast extract) were reported, which diminished with an apparent shift of the culture from DBT sensitivity to DBT adaptation and then to DBT resistance. According to the analyses of HPLC and spectrophotometry, no metabolic products of DBT transformation were identified but there was a decrease in the amount of DBT recovered and measured during adaptation stage.

This paper reports the results of cell growth and desulfurization for *S. acidocaldarius* in media containing organic sulfur compounds with and

without the presence of other organic substrates. An attempt was also made to investigate whether the desulfurization is sulfur-specific or involves degradation of the hydrocarbon moiety of the compounds.

MATERIALS AND METHODS

ORGANISM AND MEDIA:

Cultures of *S. acidocaldarius* (ATCC No. 33909, Rockville, MD) were maintained in the ATCC Medium No. 1723, hereinafter referred to as TY medium, having the following composition per liter of distilled water: $(NH_4)_2SO_4$, 1.3 g; KH_2PO_4, 0.28g; $MgSO_4.7H_2O$, 0.25; $CaCl_2.2H_2O$, 0.07 g; $FeCl_3.6H_2O$, 0.02 g; MnCl2.4H2O, 1.8 mg; $Na_2B_4O_7$, 4.5 mg; $ZnSO_4.7H_2O$, 0.22 mg; $CuCl_2.2H_2O$, 0.05 mg; $Na_2MoO_4.2H_2O$, 0.03 mg; $VOSO_4.7H_2O$, 0.22 mg; $CoSO_4$, 0.01 mg; tryptone(Difco 0123) 1.0 g; and yeast extract 0.05 g. pH was adjusted to 2.5 with H_2SO_4 before sterilization.

Other media used in the study were formed by supplementing a basal medium with tryptone/yeast extract and/or organic sulfur compounds. The basal medium had the following composition, per liter of distilled water: NH_4Cl, 0.523 g; KH_2PO_4, 0.28 g; $MgCl_2.6H_2O$, 0.2 g; $CaCl_2$, 0.106 g; $MnCl_2$, 0.8 mg; B_2O_3, 3.1 mg; and other trace elements as stated in the above TY medium. The basal medium was deficient in both carbon and sulfur sources. pH of the medium was adjusted to 2.5 using 10N HCl solution.

EXPERIMENTAL PROCEDURE:

An initial study on the desulfurization of DBT, PS and BS were carried out in 500-mL Pyrex flasks. A New Brunswick Gyratory Shaker (Model No: G76) was used to perform the experiment at 200 rpm and 70^0C. 200 mL of the basal medium was used for DBT and PS and 100 mL was used for BS. DBT was added in powder form with an initial concentration of 300 mg/L. PS and BS were added as liquid droplets with the concentration of 300 μL/L. Inocula were prepared from the centrifuged and twice-washed cells which were previously grown in the TY medium and harvested at the late exponential growth phase. Cell-free controls were also made. Samples (5 mL) were withdrawn periodically for determination of the cell concentration. The supernatant of centrifuged samples was stored in the refrigerator and analyzed for sulfate ion concentration at the end of run. A specific run was conducted with 200 mL of TY medium added with 300 μ L/L. of PS for the purpose of determination of metabolic products.

Based on the initial results, experiments with DBT were further carried out in three phases in a 7-L Microferm fermentor (New Brunswick Scientific Co.) equipped with pH probe and controller and dissolved oxygen probe. Since the maximum temperature attainable by the fermentor is about 60^0C, the optimum fermentor temperature of 70^0C was obtained by an external heating tape with a controller (Omega Engineering Inc.).

PHASE I: An extremely low cell concentration (6 mg cell dry wt./L) was used as the inoculum, which was pre-grown in the TY medium, centrifuged and washed twice in basal medium. Three liters of the basal medium were added to the fermentor and supplemented with 90 mL of *n*-hexadecane which contained 1.5 g of dissolved DBT. The experiment was carried out for 27 days and the cell viability at the end of the run was examined by Epifluorescence Microscopy (EFM) (Zeiss, West Germany) and also by transferring the cells to a fresh TY medium. Samples were collected periodically and analyzed for sulfate ion concentrations.

PHASE II: A higher cell concentration (147 mg/L) was added to the fermentor to examine the capability of the system to support high cell concentrations and to determine the variation of sulfate release rate with cell concentration. This part of the experiment was conducted as a continuation to Phase I by simply adding more pre- grown cells to the fermentor at the end of Phase I. The experiment was conducted for a period of 35 days.

PHASE III: In contrast to Phases I & II, the third phase of the study was conducted to investigate the transformation of DBT by cells cultivated in the basal medium supplemented with complex organic substrates of 1 g/L tryptone and 0.05 g/L yeast extract. Five liters of the medium added with 100 mL of *n*-hexadecane containing 1.19 g of dissolved DBT were introduced to the fermentor. Cells were inoculated at 7 mg/L. DBT concentrations in the samples were measured using GC/MS.

ANALYSIS:

The cell concentrations of the samples were determined with a spectrophotometer (Perkin Elmer Lambda 3B) by measuring the optical densities at 600 nm. Cares were taken to minimize the interference from oil droplets. Direct cell counts using a Petroff-Hausser counting chamber were also obtained initially to ascertain the adequacy of the technique. Viability of the cells was assessed by observing the sample stained with acridine orange under an epifluorescence microscope (EFM). Green-yellow fluorescence corresponded to viable cultures, while orange-red fluorescence indicated a low level of culture viability (10,11). Sulfate concentrations were analyzed according to an ASTM method (12), which converted sulfate ions to barium

sulfate colloids. The resulting turbidity was determined by a spectrophotometer and compared to a curve prepared from standard sulfate solutions.

DBT concentrations were measured using a GC/MS (Hewlett Packard 5890 GC with a 5970 series Mass Selective Detector). The column used was a 12m x 0.2 mm x 0.33 μm ULTRA-1. The oven temperature was programmed as follows: 120^0C injection, 15 deg/min to 280^0C. An attempt to identify the metabolites was also made, with another GC/MS system (HP 5890 series II GC with a 5971 series Mass Selective Detector). The samples (aqueous medium) were centrifuged and the supernatants were acidified to pH 1 with hydrochloric acid and extracted with a fixed amount of ethyl acetate. The ethyl acetate extracts were dried with anhydrous calcium chloride, filtered, and concentrated. On-column injections were utilized for sample introduction and the oven temperature program was as follows: 120^0C, 10 deg/min to 250^0C. The column used was a 12m x 0.2m x 0.33μ m HP1 cross linked methysilicone gum column.

RESULTS AND DISCUSSION

The results of sulfate release and the typical trend of cell concentration variation observed in the experiments conducted with inoculated shaker's flasks for DBT, PS and BS are shown in Figure 1. No release of sulfate or other changes in the physical appearances of the organosulfur compounds were observed in the cell-free controls, in agreement with the literature report (4). Desulfurization of these organosulfur compounds by *S. acidocaldarius* is therefore clearly indicated. This is further supported by the observation of color change and gradual disappearence of the PS droplets in the culture flasks. The desulfurization was, however, incomplete and the decrease of cell concentrations indicated the inability of these compounds in supporting cell growth in the shaker's flasks.

The results of phase I run in fermentor with DBT are summarized in Figure 2. The growth of cells over a period of 27 days in the medium containing DBT as the only source of organic carbon and sulfur was confirmed with both optical density measurements and the direct cell counts using a Petroff-Hausser counting chamber. The growth was, however, extremely slow with an average doubling time of 3.5 days and the growth stopped at a cell concentration of 42 mg/L without apparent problems in the fermentation conditions. A slight increase in sulfate concentration in the medium was also observed. Viability of the cells at the end of run was also examined using EFM which gave green-yellow fluorescence indicating that the cells were metabolically active. Active cell growth were also observed when the cells taken at the end of the run were transferred to a fresh TY medium in a shaker's flask.

The results of phase II are summarized in Figure 3. Following the addition of cells to raise the concentration to 147 mg/L, the cell concentration dropped rapidly until the final concentration reached a steady value of 44 mg/L which was about the same as the steady value of 42 mg/L obtained in Phase I. Together with the results in phase I, this ruled out the possibility of accumulation of toxic metabolites being responsible for the low cell concentration supportable by the cultivation system. The slow mass transfer of DBT from the oil phase to cells in the aqueous medium was a much more plausible controlling factor to yield the same steady cell concentration in both Phases I and II. The mass transfer capability of shaker's flasks is much poorer than that of the vigorously agitated fermentor. The continuous decrease of cell concentration in the flasks to levels much lower than the steady concentration supported by the fermentor is therefore understandable. The initial sulfate release rates in Phase II study were found to be much higher than those in Phase I, apparently due to the presence of high cell concentrations despite the rapid cell death observed during this transition.

In Figure 4, the time profiles of cell growth and DBT transformation observed in Phase III study were presented. The DBT concentration in hexadecane dropped from 11,859 mg/L to 6359 mg/L over a period of 18 days. It should be noted that the active cell growth observed in this experiment was supported predominantly, if not completely, by tryptone and yeast extract present in the medium. The sulfate release profile, estimated from the change in DBT concentration measurements, is also presented in Figure 4 for comparison. Direct measurements of sulfate concentration were not made because the presence of tryptone and yeast extract, which also contained reduced sulfur, in the medium would render the attribution of the increased sulfate concentration to sulfur release from DBT unreliable.

The results indicated higher specific DBT degradation rates during the growth phase of cells. Nevertheless, DBT transformation proceeded well into the death phase. The desulfurization of DBT was therefore not strictly growth-associated in the system supplemented with tryptone and yeast extract. It appeared that the enzyme system responsible for desulfurization of DBT was always present irrespective of the growth mode of cells and the presence of other organic substrates, i.e. tryptone and yeast extract in the study.

Figure 5 shows the Total Ion Chromatogram of ethyl acetate extract at the end of phase III. The chromatogram indicates the formation of phenoxathiin, 2'-hydroxybiphenyl-2-sulfinic acid and 4-hydroxybenzoic acid as possible metabolic products, because none of them were found in the analysis of initial sample taken right after the inoculation. The metabolites

identified shed some light on DBT metabolism by *S. acidocaldarius* which had been totally missing before. Although the compound for peak 4 in Figure 5 was identified to be sulfinic acid, it should be noted that dibenzothiophene dioxide also exhibits similar spectra. Sulfinic acid, DBT dioxide and phenoxathiin had been identified as intermediates in the sulfur-specific pathway of DBT metabolism. Also reported was the metabolic pathway of *Breviabacterium species* that oxidized the sulfur in DBT via a sulfur specific pathway but continued to degrade DBT dioxide to sulfate and benzoate, which was eventually degraded to CO_2 and H_2O (2).

In the present case, the increase of sulfate concentration in the medium indicated the cleavage of carbon-sulfur bond and the inability to identify the product of this cleavage (i.e., hydroxybiphenyl) suggested further degradation by C-C bond cleavage. The identification of small amounts of 4-hydroxybenzoic acid supported the same. The accumulation of final product(s) of DBT degradation was not observed. Similarly the GC analysis of the extracted sample taken from the shaker's flask run containing phenylsulfide in TY medium, showed diphenylsulfoxide as a major metabolite but no final product. The possible effects of the instability of the compounds formed at the operational conditions of low pH and high temperature cannot be ruled out. Further experiments were needed to clearly establish the metabolic pathway of desulfurization by *S. acidocaldarius.*

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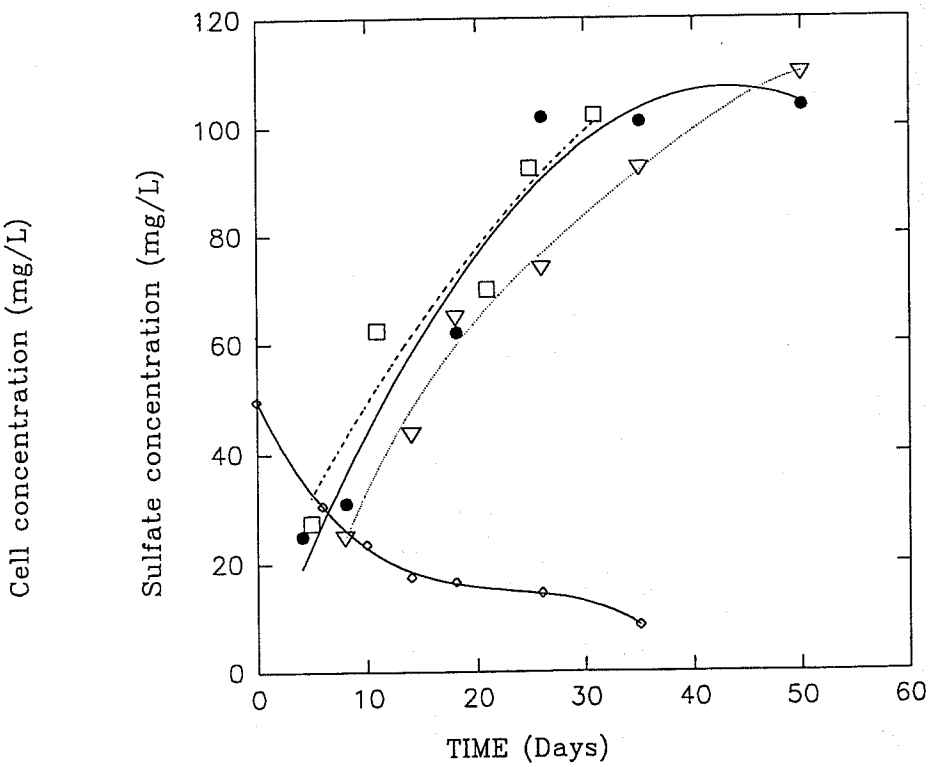


Figure 1 Sulfate release profile and variation of cell concentration in Shaker's flasks.
• sulfate release profile of DBT
∇ sulfate release profile of PS
□ sulfate release profile of BS

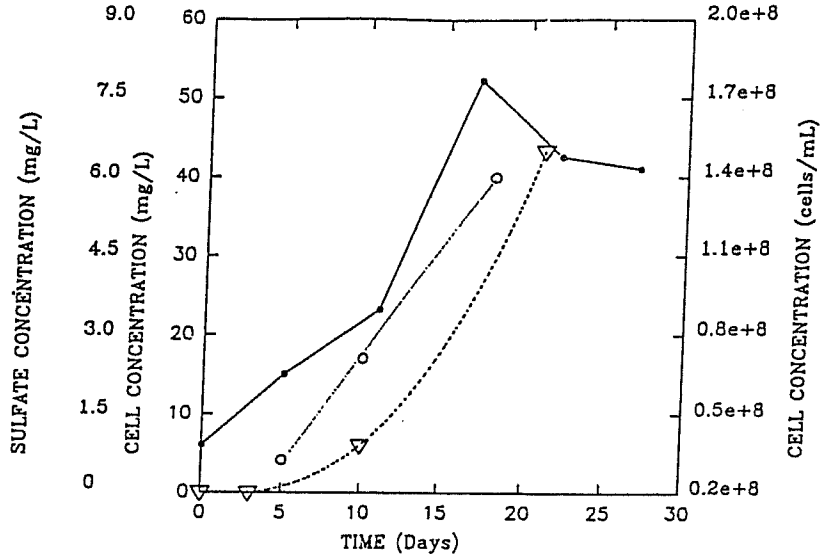


Figure 2 Profiles of cell growth and sulfate release from DBT in Phase I

- • cell concentration in mg dry cell wt./L
- ∇ sulfate concentration
- o cell concentration in no of cells/mL

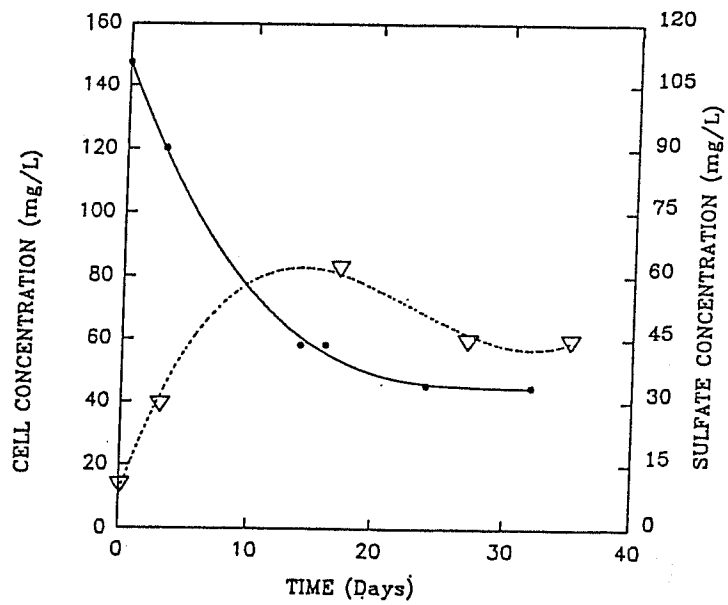


Figure 3 Inability of the system to support high cell concentration and sulfate release profile of DBT in phase II

- • cell concentration
- ∇ sulfate concentration

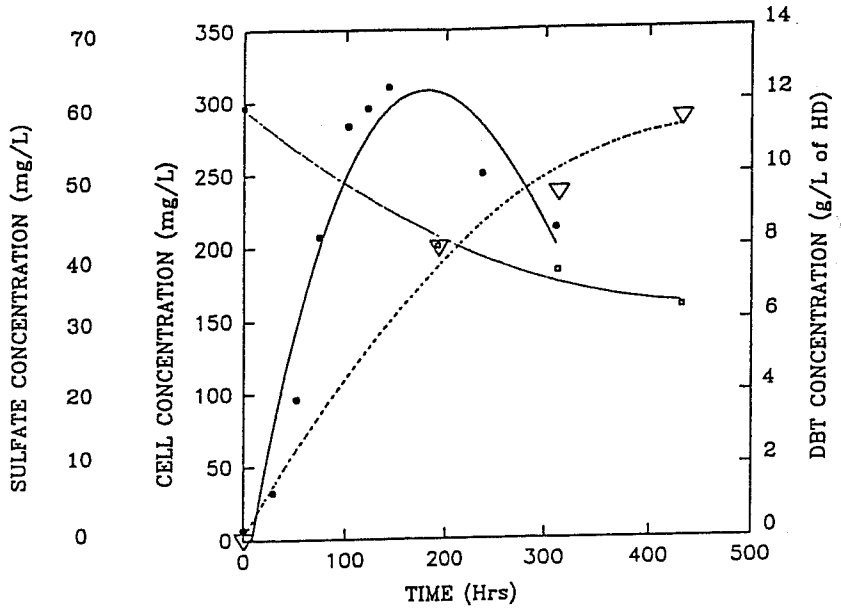
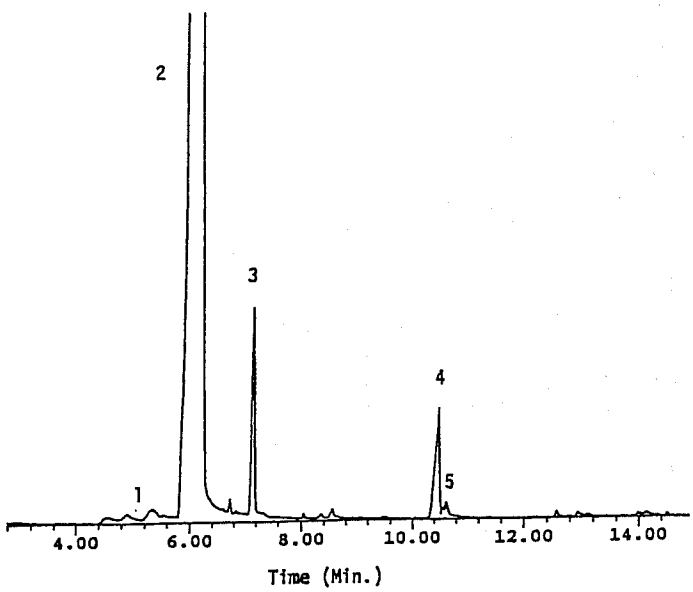


Figure 4 Growth of cells in a medium supplemented with tryptone and yeast extract in the presence of DBT and change of DBT concen. in the hexadecane phase in Phase III

- • cell concentration
- □ DBT concentration in g/L of hexadecane
- ∇ calculated sulfate concentration



(1) benzoic acid, 4-hydroxy- (2) n-hexadecane
(3) dibenzothiophene (4) sultine
(5) phenoxathiin

Figure 5 Total Ion Chromatogram of ethyl acetate extracted material at the end of Phase III

Delevopment of a Microbial Desulfurization Technology for Petroleum

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The cost to petroleum refiners of new sulfur management technology could exceed $25 billion over the next seven years and determine the fate of some small scale refiners. Conventional desulfurization technology is expensive and does not adequately handle sulfur removal in a number of situations. Biocatalytic desulfurization technology will provide a cost effective technology, competitive or collaborative with current technology, to enable refiners to meet new, lower sulfur standards even while processing higher sulfur content crudes.

In the past few years, significant progress has been made in a non-degradative, biotechnology based desulfurization process. An aerobic bacterial catalyst, which selectively breaks carbon-sulfur bonds, was isolated and characterized and the genes responsible for desulfurization were cloned and sequenced. The organism was tested with dibenzothiophene, an excellent model for the more refractory sulfur compounds in petroleum, and the pathway and intermediates identified.

In addition, several refinery materials of commercial interest have been successfully tested. A process has been designed and tested in a continuous, small scale pilot plant. A number of potential improvements to the process are currently under investigation, including very low water and immobilized catalyst systems.

Introduction

Over the last several years, the public concern over pollution, including air and water quality, has led to a variety of rules and regulations aimed at reducing the effects on the environment of burning fossil fuels. Sulfur compounds in coal and petroleum produce sulfur oxides leading to acid rain. Sulfur oxide emissions can be reduced or eliminated during or after combustion by absorbers or scrubbers. For transportation fuels, sulfur must be removed from petroleum products before use, by desulfurization. In the future, sulfur regulations will continue to pressure refiners through lower limits and greater coverages while refiners must also deal with increased pressure from the supply side, as sulfur contents of the world crude supplies increase. Refiners have been able to meet many of the sulfur regulations, including the 1993 U.S. diesel sulfur standards, with hydrodesulfurization (HDS), or by altering crude supplies, or opting out of the market. HDS uses hydrogen and a metal catalyst operating at high temperatures and pressures to produce hydrocarbons and H_2S from organosulfur compounds. A staple of refineries, HDS is not economic for gasoline stocks because it reduces octane, nor for crude oils or resids, where costs become excessive. An HDS unit may cost $40 million and additional hydrogen and sulfur plant capacities, if required, can double the cost. HDS effectively reduces light sulfur compounds, mercaptans and thiophenes, but is not as effective for heavier sulfur compounds like dibenzothiophene. Clearly, hydrodesulfurization is not the complete answer for the petroleum industry and many researchers have looked to microbes to remove sulfur from oil - biocatalytic desulfurization.

Oil can be desulfurized by a variety of organisms through pathways that actually do not remove sulfur during the conversion process. Dibenzothiophene, a compound used as a model for organosulfur compounds in coals and petroleum, can be converted to a water soluble oxygenated organosulfur compound by Reaction 1, Table I (1). The organic phase is desulfurized by breaking carbon-carbon bonds and removing the organosulfur compounds in the water phase. Unfortunately, the organisms are not selective for sulfur compounds, but for aromatics in general. So, desulfurization with those organisms will remove a significant amount of the hydrocarbon to the aqueous phase. Several investigators looked for organisms which would attack carbon-sulfur bonds, produce a desulfurized organic product, and retain most of the fuel value. John Kilbane and co-workers at Institute of Gas Technology identified an organism which did just that, IGTS8 (2). Operating on DBT, the end products were sulfate in the aqueous phase and 2-hydroxybiphenyl, Reaction 2, Table I. Additional tests at IGT and elsewhere confirmed the ability of IGTS8, tentatively identified as Rhodococcus rhodochrous (now believed to be Rhodococcus erythrypolis) to convert DBT into 2HBP and sulfate (3). Though identified in a DOE sponsored program for coal, the value of this organism for liquid fuel was strong enough to found a company, Energy BioSystems Corporation (EBC), and support private development efforts on biocatalytic desulfurization (BDS).

Process Concept

The problem presented to EBC was to take BDS from a shake flask (40 cc or so) to 40,000 barrels per day at a cost of cents per gallon. The first engineering studies provided a process concept and preliminary economics (4). The initial concept was nearly a straight translation of the shake flask to biotechnical process -

a fermentor to produce catalyst coupled directly to a continuous, stirred tank reactor where the oil was desulfurized. Most industrial fermentations are not run continuously because eliminating microbial contamination in a continuously fed process is very difficult. Rhodococccus is not a fast growing organism and contaminating organisms would soon overrun the process. However, the cells will desulfurize when in a resting state -- even cell fragments will work. Thus, production of the biocatalyst might be accomplished in a more traditional fashion, off the refinery site, and shipped to the use point -- a more workable and flexible process. The generalized process, shown in the sketch, Figure 1, was used to generate rough material balances and preliminary process economics, test hypothesis about the catalyst, define assumptions, and size equipment. Five areas of development are embodied in the conceptual process; 1) catalyst development, 2) reactor development, 3) separations, 4) by-product (salt) disposal, and 5) product quality.

Of those five, the catalyst and reactor development seemed to require the most action. The separations area encompassed not only oil/water/catalyst separations but also salt rejection and exhaust gas clean-up (VOC's). We believe separations can be handled by application of appropriate, existing technologies. For example, a disc-stack, split bowl centrifuge will separate the oil/water/cell mixture into a clean oil stream, a clean water stream, and a concentrated cell slurry under many operating scenerios. The choice of by-product salt disposal is currently between sodium, ammonium, or calcium sulfate, but will be site-specific and depend on markets and local regulations. We do not anticipate product quality issues to be severe, but BDS will increase the oxygen content of the hydrocarbon stream. The product quality issue will depend on the specific stream and how close it is to a finished product when biodesulfurized.

To shorten the development time, we are developing the catalyst and process steps in parallel. By working on both programs simultaneously, we hope to feed information back and forth to strengthen both areas through the needs and limitations of the other. The initial target refinery stream could dictate a great deal of the catalyst and process development activities and we were concerned that choosing only one fuel would lead to a too narrow focus. We were also aware that while we could not ignore the variety of refinery streams out there, we could not concentrate on all of them at the same time. We instituted a core development program to concentrate first on the model system - the DBT to 2-HBP reaction - and one real fuel, a middle distillate. The middle distillate is in the middle of the fuel product boiling point range and is a major component in diesel fuel. It has substantial paraffinic, naphthenic, and aromatic content and is a reasonable sulfur target - many DBT-type compounds with a total sulfur content of about 0.75 wt. %. Evaluation of the middle distillate requires a total sulfur analysis and a GC with a sulfur specific detector. Even then, oxygenated products cannot be determined with accuracy - there is no oxygen detector for the GC and the products will be produced in quantities too small to show up in GC flame ionization detector (FID) spectra.

The focus on commercialization targets is being handled by Accelerated Development Programs, or ADPs. Each ADP involves laboratory work on a single stream from a single refinery and focuses on the specific development requirements posed by that stream. Two ADPs have been announced to date, the first on a crude oil and the other on light coker naphtha. Major issues with crude appear to be the range of hydrocarbons and viscosity of the oil. Light coker naphtha is a very light

hydrocarbon mixture with sulfur predominately as mercaptans and thiophenes. At the appropriate times, determined by results of the experimental program and preliminary engineering, each of these ADPs will be integrated into the core development program through pilot plant runs and advanced engineering.

A model system - 3 wt. % DBT (about 0.5 wt. % S) in hexadecane was used for much of the difficult, basic laboratory work. The model system has an advantage over middle distillate in that it never contains more than three components - hexadecane, DBT, and 2-HBP. The concentrations of those materials can be determined accurately and quickly in a GC equipped with a flame ionization detector (FID). Also, hexadecane (common name cetane) is a good surrogate for middle distillate - the cetane index is a measure of diesel quality just as the octane number describes gasoline quality.

Catalyst Development

The heart of this process is the biocatalyst. The most important aspects of the catalyst are its selectivity, its activity, and its longevity. There is no evidence of the ring-opening oxidation reactions (reaction 1) by IGTS8. The reaction was defined at EBC and elsewhere for a Corynebacterium (5) to produce sulfite and subsequently, sulfate, Reactions 3a and 3b, Table I. Under normal reaction conditions, oxidation of sulfite is rapid enough that only sulfate is detected. The other side of selectivity - the ability of the enzyme system to break all carbon-sulfur bonds has been probed but not explored in depth. The catalyst was screened for activity with a variety of organosulfur compounds by a sensitive sulfite assay, Table II. (The catalyst was checked for activity on over 75 compounds, many not of interest in the context of petroleum.) Many compounds, including thiophenes and benzothiophene were attacked by the catalyst, but the study suggested that the catalyst is currently more effective on dibenzothiophene and thianthrene. The overall rate of sulfur removal from a refinery stream will depend on the nature of the sulfur compounds present and their concentrations.

The effectiveness of the catalyst will also depend on the specific activity and the maintenance of that activity through time in the process. The specific activity of the catalyst is the number of conversions a given amount of catalyst can facilitate in a unit of time (we normally use mg 2HBP/hr/g dry catalyst weight). The specific activity of the wild type IGTS8 was less than 1. Fermentation optimization in the laboratory produced cells with activities of 25 to 30 from shake flasks. 400 L fermentation runs produced kilogram quantities of the catalyst with activities routinely at 4 to 6, but occasionally to 8 or 10, for engineering studies. Fermentation development alone will not yield catalyst activities in the range of 600 to 3000 needed for commercialization. Alteration of the organism itself is required.

The two techniques used are mutation/selection and the modern techniques of genetic engineering. Mutation has produced some interesting and useful tools for research, but we have not yet pushed the process far enough to produce a super active organism. We committed a majority of our efforts to genetic engineering. The gene cluster responsible for the desulfurization phenotype has been isolated, sequenced, and cloned.(6) Desulfurization negative R. erythrypolis and R. faciens have been converted to desulfurization positive strains and the genes have been

expressed in E. coli to produce a desulfurization positive organism. The gene cluster contains three open reading frames which code for three gene productes - the enzymes necessary for desulfurization. One of those three is believed to code for the enzyme which catalyzes the conversion of DBT to DBT-sulfoxide and DBT-sulfone, Reaction 4, Table I. We believe another enzyme converts sultine to 2-hydroxybiphenyl, Reaction 5, Table I. The function of the third may be to rearrange DBT sulfone to the sultine. We have identified DBT sulfoxide and sulfone in reaction media but have not located any other intermediates. The sultine is not stable in aqueous media and may not be released by the enzyme system. Several researchers have suggested 2.2'-dihydroxybiphenyl as a reaction product via the 4S pathway.(7) To date, we have not detected 2,2'-DHBP produced from DBT in any experiment; we have detected it as a product from IGTS8 catalyzed oxydesulfurization of DBT-sultone, Table I.

The challenge in front of the molecular biologists, microbiologists, and biochemists is to gain sufficient information to engineer an organism which will express a very high desulfurization activity, is stable at reactor conditions, may be grown cheaply, and can be handled without special precautions. That work is well along and should come to at least partial fruition before the scheduled initiation of a pilot plant in late 1994. Process development must devise a process which gets the most out of the catalyst in an oil-water system at the lowest cost..

Reaction Research

An early concern in this program was how well the catalyst would perform in an aqueous/hydrocarbon environment and under conditions not conducive to cell growth and reproduction. Most of the early work was conducted with DBT in an aqueous environment. Kilbane reported positive results with coal and some oil substrates, but most of those experiments were conducted with small amounts of oil and an aqueous system which was essentially a nutrient broth.(1) To step out of the microbiology framework and into the process configuration, we needed an experimental platform more flexible and adaptable to a process configuration. We chose a stirred tank reactor operated first in the batch mode (BSR) and later in continuous feed operation (CSTR). To step out of the fermentation methodology into a process concept, we began to eliminate fermentation requirements. Other than aeration, no nutrients, trace metals, or other cell growth requirements were used in these experiments. The lab experiments look much like the reactor in Figure 1 - a four phase mixture of oil, water, cells, and air in a well stirred vessel.

We were successful in moving to a larger scale and away from fermentation requirements in the 1 liter BSR -- Figure 2 shows a plot of 2-HBP production from DBT (in hexadecane/water) in a BSR as a function of time. Parameters that appeared to be important to conversion were pH, agitation rate, aeration rate, temperature, and cell loading -- as might be expected. Conditions which favor good contact and oxygen concentration promote conversion. The pH should be between 6 and 8 and the temperature about 30° C (reasonable conversion was also measured at 40° C). BSR studies confirmed the conversion of DBT to 2-HBP, the ability of the catalyst to perform without additional nutrients and trace metals, and the importance of many process variables. In BSR and shake flask studies we also confirmed the catalyst is effective in converting DBT to 2-HBP throughout the range of DBT concentrations from 0 to 3 wt. % and capable of taking DBT to

extinction. No evidence of product (2-HBP) inhibition was found and though sulfate concentration affected conversion negatively, catalyst effectiveness was still 25% in a saturated solution of ammonium sulfate (43 wt. %).

Catalyst activity can be calculated as a function of exposure time from 2-HBP production data. The 2-HBP data from Figure 3 was converted to effective activities (relative to the specific activity measured in aqueous media) and plotted versus time, t, in Figure 3. The semi-log plot suggests the specific activity of the catalyst declines in an exponential manner,

$$SA_t = SA_0 e^{-(t/\tau)} \qquad 5$$

where τ is 11.5 hours. The mathematical expression above conforms to first order decay behavior. Typically, the value of τ varies from about 8 to as much as 16 for the model system. Maintenance of catalyst activity influences the effectiveness and cost of the process and must be maximized. No attempt has yet been made to stabilize the catalyst, either through genetic alteration, fermentation conditions, or through external stabilization efforts.

Desulfurization of Petroleum Stocks

The experiments with the DBT/2-HBP in hexadecane system were invaluable in allowing us to measure precisely the behavior of the catalyst under a variety of conditions. Refinery streams, complex mixtures of hydrocarbons with a variety of sulfur species, may not respond in the same fashion. Experiments conducted with a variety of refinery materials confirm IGTS8 is active for desulfurization under a broad range of hydrocarbon and sulfur environments. Figure 4 shows before and after sulfur specific GC spectra (flame photometric detector) for middle distillate. Total sulfur was reduced from 0.75 wt. % to 0.50 wt. % S in three successive contact stages. Figure 5 shows similar spectra for a cat cycle oil after one contact stage. These spectra (sulfur chemiluminescence detector) demonstrate about 80% desulfurization. We observed desulfurization for petroleum stocks ranging from crude oil through gasolines and light naphthas. Experiments with refinery materials and laboratory constructs indicate the rate of desulfurization is currently higher for heavier, more aromatic sulfur compounds, like dibenzothiophene, and less for lighter, paraffinic mercaptans. This enables BDS to complement HDS in some circumstances and replace it in others.

Summary

Though still not a commercial process, biocatalyzed desulfurization is a well advanced technology that should be available in the marketplace by 1995. The specific activity of the biocatalyst must be increased from the currently achieveable levels of 25 (mg 2-HBP/hr/g dry cell weight) to levels in excess of 600. While fine tuning the fermentation process will probably not give such an increase, genetic engineering should. The half-life of the catalyst can also be improved, from about 10 hours to 20 hours or more. Again, though not yet achieved for this system, that goal seems attainable and we are just beginning to address that issue in the laboratory. The catalyst cells show a broad based activity toward many different

types of sulfur compounds and there is no indication that they catalyze any reaction other than desulfurization.

Experiments in BSRs have allowed us to determine the biocatalyst response to operating variables and to develop a model based on analysis of those responses. The commercial process will not be a batch process, but a continuously fed reactor with catalyst recycle. Based on the BSR work, we are able to predict process performance in a continuous system and look at a more controlled system in steady state operation rather than the transient behavior observed in a batch system. Continuous experiments confirmed the concepts developed from the batch experiments and have allowed us to scale up to a pilot plant with a planned capacity of 1 barrel (42 gal.) of oil per day by the fourth quarter on 1994. The Accelerated Development Programs will also lead to pilot runs and one of those programs may lead to an early commercial plant. At the same time, process improvements are being aggressively pursued in the microbiology and biochemistry areas and in engineering. More robust organisms with higher activities, more solvent resistance, or different selectivities are being sought to work alone or with the current catalyst. Novel reactor designs, low water systems, and anaerobic/aerobic combination processes are being investigated.

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Table I

Biocatalyzed Reactions of Dibenzothiophene and Intermediates

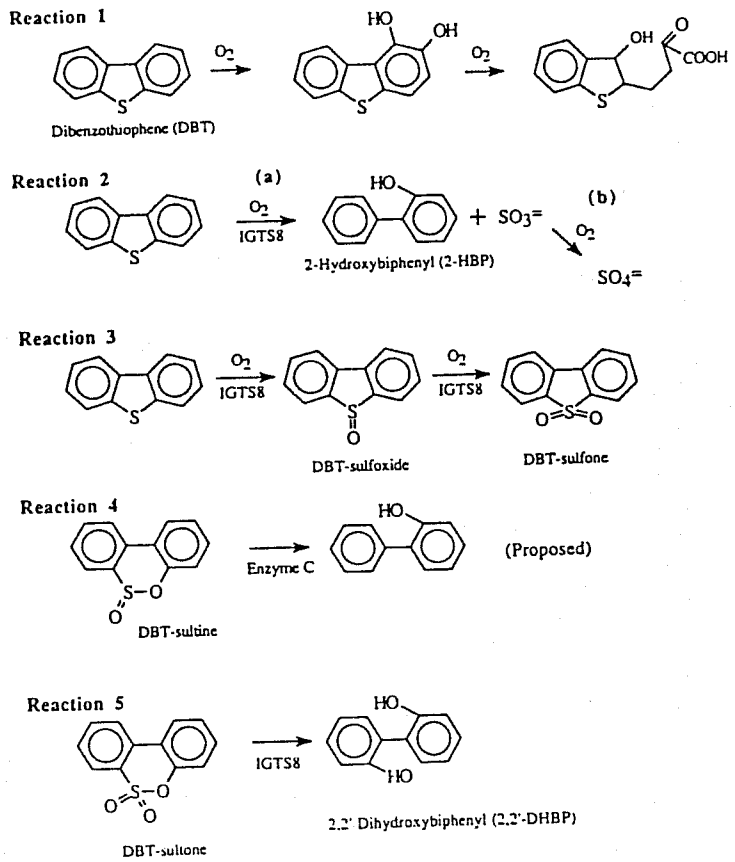

Table II

Effectiveness of IGTS8 for Desulfurization of Sulfur Compounds Relative to Its Effectiveness Against Dibenzothiophene *

Sulfur Compound	Effectiveness
Dibenzothiophene	100
Thianthrene	62
Dibenzosulfone	58
4,4' thiodiphenyl	45
3 methyl thiophene	22
2 ethylthiophene	18
thiophene	16
benzyldisulfdide	14
trithiane	12
2,5 dimethyl thiophene	12
phenyl disulfide	8
2 methylthiophene	6
benzothiophene	6
dimethyl sulfoxide	2

* Determined by amount of $SO_3^=$ detected by aqueous assay

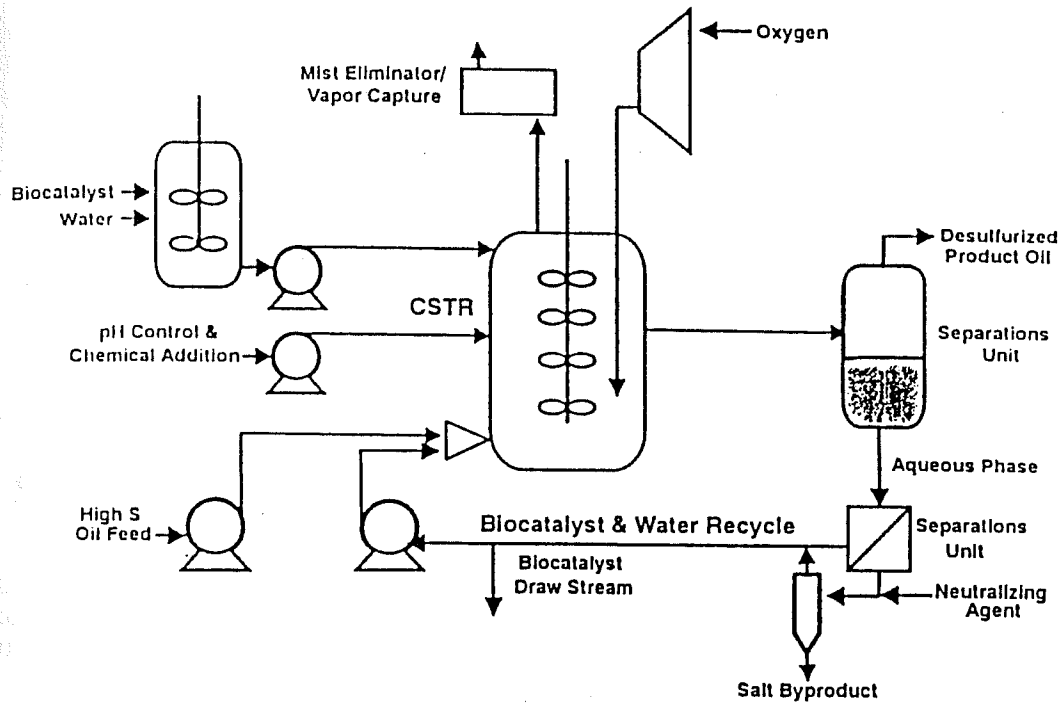

Figure 1 Process schematic for a petroleum bodesulfurization process.

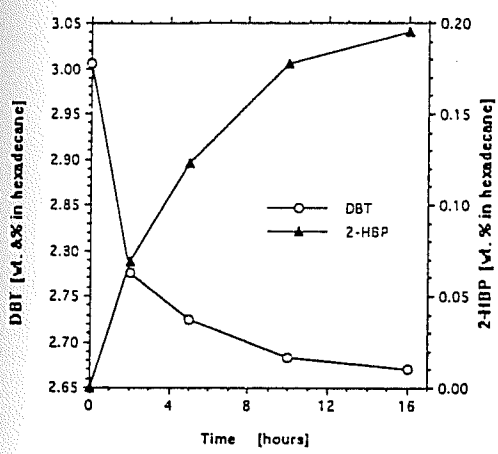

Figure 2 Production of 2-HBP from dibenzothiophene in a batch stirred reactor (BSR). The reaction was catalyzed by whole IGTS8 cells in an aerated hexadecane/water mixture without additional nutrients or trace metals.

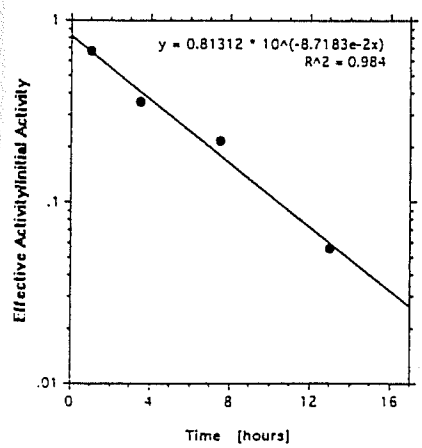

Figure 3 2-HBP production data from Figure 2 yields an effective catalyst activity which suggests an exponential decline in activity with time.

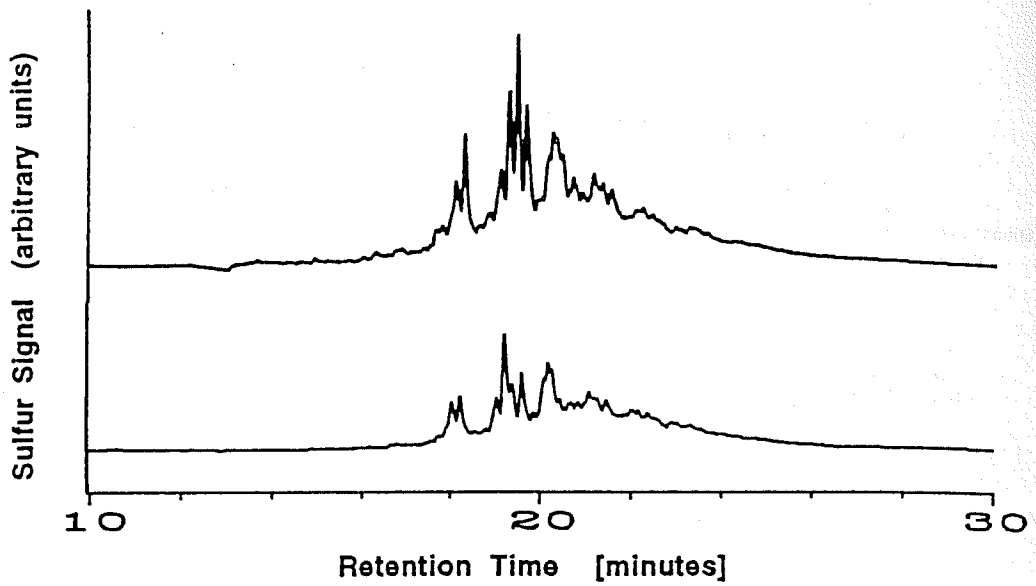

Figure 4 GC spectra of middle distillate before (top) and after three contacts (bottom) in batch stirred reactors with IGTS8 whole cell catalyst. A sulfur specific detector was used for these traces. Total sulfur was reduced from 0.75 wt. % to 0.50 wt. %.

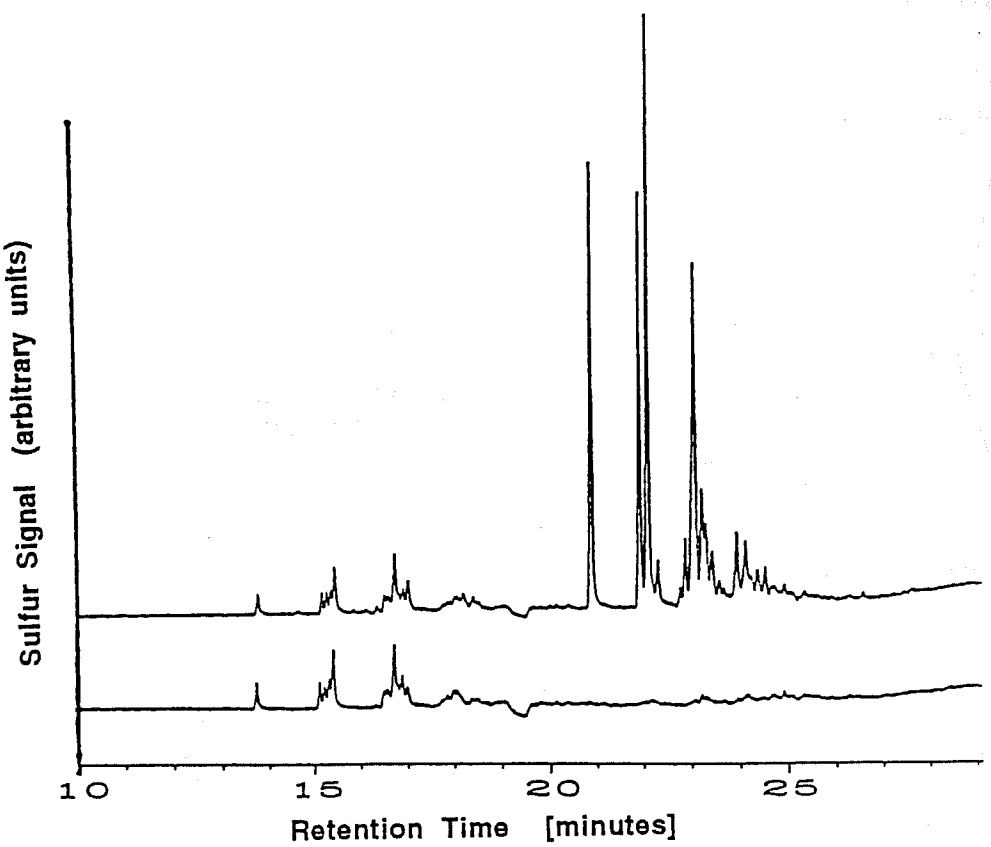

Figure 5 Approximately 80% of the sulfur was removed from a mid cat cycle oil in one contact with IGTS8 in a BSR. The GC spectra shown here were from a sulfur chemiluminescence detector.

Bacterial Oxidation of Organosulfur Compounds Found in Petroleum

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Abstract

Although there are hundreds of organosulfur compounds in petroleum, only about 20 of these are commercially available. Therefore, few pure organosulfur compounds have been used in biodegradation studies to help assess their environmental fates. We have synthesized nearly 30 organosulfur compounds and used these for biodegradation studies. Of those tested, only the *n*-alkylthiophenes supported bacterial growth in pure cultures, and the side-chains, that ranged up to 16 carbons in length, were removed leaving thiophenecarboxylic acids. The condensed thiophenes were biotransformed by *Pseudomonas* spp. grown on 1-methylnaphthalene or glucose. Sulfoxides and sulfones were common metabolites from benzothiophenes, methylbenzothiophenes, and methyldibenzothiophenes. Methylbenzothiophene-2,3-diones were formed from some methylbenzothiophenes and from methyldibenzothiophenes. Several investigators have demonstrated the bacterial production of 3-hydroxy-2-formylbenzothiophene (HFBT) from dibenzothiophene. Similarly, methylHFBTs were metabolites of the methyldibenzothiophenes. Two bacterial isolates oxidized the methyl groups of the methylbenzothiophenes and methyldibenzothiophenes to the corresponding alcohols and carboxylic acids.

INTRODUCTION

Although hundreds of organosulfur compounds have been identified in petroleum, a recent literature review (1) showed that fewer than 20 of these compounds had been subjected to biodegradation studies. Thus, little is known about the fate of organosulfur compounds in petroleum-contaminated environments.

The removal of organosulfur compounds from petroleum has been demonstrated in laboratory biodegradation studies (2-4), but the identities of the metabolites were not determined because of the complex mixture of compounds in the oil. The identification of microbial metabolites is most easily done with pure compounds in laboratory cultures. However, the lack of commercially available

model compounds has hampered studies of the transformations of petroleum-related organosulfur compounds. Indeed until recently, the few organosulfur compounds that had been studied were those that are commercially available. Thus the only means by which a more complete understanding of the microbial metabolism of organosulfur compounds can be achieved is through the collaboration between chemists who synthesize the organosulfur compounds and microbiologists who carry out the biotransformation studies. We have been studying the aerobic microbial transformations of synthesized organosulfur compounds for several years, and the following compounds have been investigated: alkylthiophenes (5), methylbenzothiophenes (6) and methyldibenzothiophenes (7).

Some aerobic microorganisms can use dibenzothiophene as their sole carbon and energy source (8-10), but much research has shown that condensed thiophenes are biotransformed aerobically while the microorganisms are growing at the expense of another carbon source (11-13). That is, the condensed thiophenes are fortuitously oxidized, rather than being mineralized (1, 14).

The main goal of our ongoing investigations is to gain a better understanding of the metabolic activities of microorganisms grown in the presence of organosulfur compounds that are found in petroleum. The major focus of these studies is the identification of the oxidation products of these biotransformations. Special attention is given to the microbial formation of sulfoxides because, in the few cases studied, these have been shown to be more mutagenic than the parent thiophenes (15). This paper presents the identities of a variety of microbial oxidation products from alkylthiophenes, methylbenzothiophenes and methyldibenzothiophenes.

MATERIALS AND METHODS

Chemicals

The alkylthiophenes and the synthesis methods used have been previously published (5). Benzothiophene and 3-methylbenzothiophene were purchased (13), and the methods for the syntheses of methylbenzothiophenes and methyldibenzothiophenes are given elsewhere (16), and (7), respectively. Fig. 1 shows the general structures of the compounds studied. Benzothiophene sulfoxide and 4-methyldibenzothiophene sulfoxide were prepared in analytical amounts by oxidizing benzothiophene and 4-methyldibenzothiophene, respectively, using cytochrome c and H_2O_2 (17). 2-Benzothiophenecarboxylic acid was also synthesized (18).

Bacterial cultures

Six Gram-positive *n*-alkane-degrading bacteria were used in the studies with the alkylthiophenes, in addition to a mixed culture of oil-degrading bacteria, designated SLPB (5). Three *Pseudomonas* strains, each enriched on 1-methylnaphthalene, were used in the studies with the condensed thiophenes. Isolate BT1 came from the SLPB mixed culture (13). Strains W1 and F were enriched from a freshwater tropical aquarium, and from domestic activated sludge, respectively (7).

Culture methods and medium

Cultures were routinely grown at 28°C in shake-flasks containing 200 mL of liquid mineral medium (3) supplemented with a trace metals solution (13). For studies with the condensed thiophenes, 1-methylnaphthalene or glucose was used as the growth substrate at a concentration 50 mg per 200 mL of medium. The

amounts of organosulfur compounds added to the cultures ranged from 3 to 10 mg. In some experiments, 0.2 mL of Prudhoe Bay crude oil were added to the medium. For each biotransformation experiment, a sterile control, consisting of autoclaved growth medium and the appropriate substrate, was incubated and analyzed in the same manner as the active culture to account for any abiotic transformations.

Analytical methods

After incubation, the cultures were acidified with sulfuric acid to pH<2 and extracted with CH_2Cl_2 (4 times 20 mL) to recover substrates and products. Extracts were analyzed by gas chromatography (GC) (13). The method for GC-mass spectrometry (GC-MS) is given elsewhere (6, 19). GC-Fourier transform infrared spectroscopy (GC-FTIR) analyses were done in the Spectral Services Laboratory, University of Alberta (13). To facilitate GC-MS identification of some of the metabolites, trimethylsilyl (TMS) derivatives of compounds in culture extracts were made by silylating with *N,O*-bis(trimethylsilyl)acetamide (BSA) in acetonitrile according to the manufacturer's instructions (Pierce, Rockford, IL; method 5).

RESULTS AND DISCUSSION

Biodegradation of alkylthiophenes

Six alkylthiophenes were synthesized and studied for their biodegradability (5). Of these, 2-hexadecyl-5-methylthiophene (Fig. 2, compound **d**) was prepared in the largest quantity (700 mg) and it was studied most extensively. The results from this work are presented here. Pure culture experiments showed that compound **d** supported growth of *n*-alkane-degrading bacteria, and after 28 days incubation yielded two sulfur-containing metabolites that were identified as 5-methyl-2-thiophenecarboxylic and 5-methyl-2-thiopheneacetic acids (Fig. 2) by GC-MS analysis (5). The latter metabolite was the more abundant and it would arise from the initial oxidation of the methyl group on the hexadecyl side chain and subsequent beta-oxidations removing seven acetate molecules, leaving 5-methyl-2-thiopheneacetic acid. A decarboxylation would yield 5-methyl-2-thiophenecarboxylic acid. These two acids were not metabolized further by the pure cultures tested.

In general, pure culture studies with the other five alkylthiophenes showed similar results (5). That is, the longer side chain, whether alkyl or isoprenoidal, was attacked and degraded leaving 5-alkyl-2-thiophenecarboxylic acid or 5-alkyl-2-thiopheneacetic acid. The one exception was the isopenoidal compound, 2-(3,7-dimethyloctyl)-5-methylthiophene, in which the 5-methyl group was oxidized to give 2-(3,7-dimethyloctyl)-5-thiophenecarboxylic acid (5).

When the mixed culture SLPB was grown on compound **d** alone, 5-methyl-2-thiophenecarboxylic and 5-methyl-2-thiopheneacetic acids accumulated in the medium (5). However, when a mixture of compound **d** and Prudhoe Bay crude oil were incubated for 14 days with the mixed culture, these thiophene-containing products were not found. Thus, some components of the oil stimulated the further biotransformation of these metabolites. When the mixed culture was incubated with 5-methyl-2-thiophenecarboxylic acid and *n*-hexadecane (in place of the oil), both were depleted from the medium. Thus, the *n*-alkane stimulated the biotransformation of the thiophenecarboxylic acid. However, the transformation products have not been detected.

Biotransformations of benzothiophene and methylbenzothiophenes

Biotransformations of two commercially available organosulfur compounds, benzothiophene and 3-methylbenzothiophene were initially studied using a 1-methylnaphthalene-utilizing bacterium, *Pseudomonas* sp. BT1 (13) and the predominant metabolites were benzothiophene-2,3-dione and 3-methylbenzothiophene sulfoxide, respectively (Fig. 3). 3-Methylbenzothiophene also yielded a small amount of its sulfone. The identities of the dione and the sulfone were confirmed by comparison of GC-MS data with those of synthesized standards. The sulfoxide could not be synthesized, so its identity was determined from GC-MS and GC-FTIR data (13).

These findings lead to the prediction that if a methyl group was on the benzene ring, the corresponding 2,3-dione would be formed, whereas if a methyl group was on the thiophene ring of benzothiophene, the corresponding sulfoxide and sulfone would be formed. Further studies with isolate BT1 (6) showed that this prediction was generally true (Table 1). One exception was the formation of the sulfoxide, sulfone and dione from 7-methylbenzothiophene. *m*-Tolyl methyl sulfoxide, *m*-$CH_3C_6H_4(S{=}O)CH_3$, was found in the extract from the culture with the mixture of 4- and 6-methylbenzothiophenes (the synthesis of the latter compound gave a mixture of the two isomers). This was the only metabolite detected that had the thiophene ring cleaved, and it was produced from 6-methylbenzothiophene, because it was not found in cultures that contained only 4-methyl isomer.

In a subsequent investigation (20), two different *Pseudomonas* isolates were studied to determine whether they produced the same oxidized products as isolate BT1. The results of this work are also summarized in Table 1. Many of the metabolites were the same, but some novel products were found. For example, when incubated with benzothiophene, isolates W1 and F yielded two new metabolites, along with the 2,3-dione. The mass spectra of these new products are shown in Fig. 4. One was identified benzothiophene sulfone by comparison with a synthesized standard, and the other was identified as benzothiophene sulfoxide on the basis of its mass spectrum.

During growth on 1-methylnaphthalene, isolates W1 and F oxidized a fraction of this substrate to 1-naphthalenemethanol and subsequently to 1-naphthoic acid which was a dead end product (7). These bacteria also oxidized the methyl group of some of the methylbenzothiophenes to yield the corresponding methanols and carboxylic acids (Table 1). Fig. 5A shows the mass spectrum of the TMS-derivative of a metabolite formed by isolate F from 2-methylbenzothiophene. Its GC retention time and mass spectrum matched those of the TMS-derivative of 2-benzothiophenecarboxylic acid. In addition, Fig. 5B shows the mass spectrum of the TMS-derivative of a metabolite of 3-methylbenzothiophene produced by isolate F. The metabolite was tentatively identified as 3-benzothiophenemethanol.

Isolates W1 and F also produced a novel metabolite from 7-methylbenzothiophene. GC-MS analysis showed the molecular ion at *m/z* 154. This ion and the major fragment ions at *m/z* 65, 77, 91, and 111 were also found in the mass spectrum of *m*-tolyl methyl sulfoxide (6). The FTIR spectrum of the metabolite from 7-methylbenzothiophene was very similar to FTIR spectrum of *m*-tolyl methyl sulfoxide (6), showing a strong absorption at 1095 cm^{-1} which is characteristic of a sulfoxide (21). A portion of the culture extract was oxidized with H_2O_2 in acetic acid, and GC-MS analysis showed that the sulfoxide was absent and that a new product with a molecular weight of 170 had formed. This was 16 mass units greater than the sulfoxide, and was the corresponding sulfone indicating that this metabolite

was *o*-tolyl methyl sulfoxide, *o*-$CH_3C_6H_4(S{=}O)CH_3$, which resulted from the cleavage of the thiophene ring.

Biotransformations of methyldibenzothiophenes

All four isomers of methyldibenzothiophene were synthesized and used as substrates for the three *Pseudomonas* isolates grown on 1-methylnaphthalene or glucose. The synthesis method for 1-methyldibenzothiophene yielded a mixture of 1- and 3-methyl isomers. The metabolites formed from 4-methyldibenzothiophene by isolate W1 are discussed in detail because of the availability of reference compounds that helped to identify the oxidation products (Fig. 6), and because this isolate produced the largest number of metabolites from this isomer.

Each of the isolates produced 3-hydroxy-2-formylbenzothiophene (HFBT) from dibenzothiophene (7). GC-MS analysis of an extract of isolate W1 grown with 4-methyldibenzothiophene showed several sulfur-containing metabolites. One had a molecular weight of 192, 14 mass units greater that HFBT, suggesting that it was 7-methyl-HFBT. This metabolite could be partially purified by extracting it from a CH_2Cl_2 solution into 5% $NaHCO_3$ solution in the same manner that HFBT could be removed from a CH_2Cl_2 solution (1). The partially purified product was analyzed by thin layer chromatography (7), giving a spot that fluoresced blue under long-wave-UV light, as does HFBT (7). HFBT and the metabolite both gave positive reactions with Gibb's reagent and *o*-dianisidine, confirming the presence of an aromatic alcohol and an aldehyde, respectively. Although no authentic standard was available, all of the data are consistent with the metabolite being 7-methyl-HFBT.

Another metabolite had a weak molecular ion at *m/z* 178, suggesting that it was 7-methylbenzothiophene-2,3-dione which was an oxidation product of 7-methylbenzothiophene (Table 1). This dione was synthesized and it gave the same MS and FTIR spectra as the metabolite, confirming the identity of this product.

GC-MS analysis of this culture extract also showed two oxidation products from 4-methyldibenzothiophene that had molecular ions at *m/z* 214. The following reactions would yield metabolites with this molecular weight: oxidation of the sulfur atom to give the sulfoxide; oxidation of the methyl group to yield the methanol; and oxidation of one of the carbon atoms in an aromatic ring to yield a phenol. 4-Methyldibenzothiophene sulfoxide was synthesized and its mass spectrum and GC retention time were compared to those of the metabolites. These did not match (7), so neither of the metabolites was the sulfoxide.

4-Dibenzothiophenemethanol was a gift from Dr. A.R. Katritzky (Univ. of Florida, Gainesville, FL). The mass spectrum and GC retention time of this reference compound matched those of one of the metabolites. Thus, isolate W1 oxidized the methyl group of 4-methyldibenzothiophene in the same manner as it oxidizes the methyl groups of 1-methylnaphthalene and some of the methylbenzothiophenes (Table 1).

Because of its relative ease of preparation, 2-hydroxy-8-methyldibenzothiophene was synthesized (7). The mass spectrum of one of the oxidation products with molecular weight 214 matched that of the synthesized compound (7), suggesting that the former was an isomer of hydroxy-4-methyldibenzothiophene. But, the position of the hydroxy group is not known, so the designation "x-hydroxy-4-methyldibenzothiophene" was used in Fig. 6. The final metabolite from 4-methyldibenzothiophene detected in the culture extract of isolate W1 had a molecular weight

of 230, which was consistent with it being the sulfone of the substrate. Indeed, its mass spectrum matched that of synthesized 4-methyldibenzothiophene sulfone (7).

Table 2 summarizes the metabolites found in extracts of the three *Pseudomonas* isolates grown in the presence of each of the methyldibenzothiophenes. Sulfones were detected only in cultures that received 2- or 4-methyldibenzothiophenes, whereas methylbenzothiophene-2,3-diones, methyl-HFBTs, dibenzothiophenemethanols and hydroxymethyldibenzothiophenes were detected from each of the four methyldibenzothiophenes. The formation of monohydroxy-substituted metabolites was unexpected because bacterial metabolism usually occurs via catechol formation (22), whereas fungi and higher eukaryotes are known to produce monohydroxylated aromatic compounds. The monohydroxymethyldibenzothiophenes detected in this study may have been formed by the dehydration of the corresponding dihydrodiol under the acidic conditions used during the extraction procedure.

Implications for bioremediation

One of the driving forces behind the studies of biotransformations of compounds in petroleum is to better understand the feasibility of bioremediation in environmental cleanup. This systematic investigation has identified numerous microbial metabolites of alkylthiophenes, benzothiophenes and dibenzothiophenes that form in laboratory cultures. Although, the direct implications of these results to bioremediation programs is not currently evident, the accumulation of these metabolites in the culture media serves as a reminder that the loss of a compound from an environment may be due to minor biotransformations rather than complete biodegradation.

Typically, the effectiveness of a bioremediation program is assessed by monitoring the loss of selected compounds, such as the U.S. EPA priority pollutants. However, it is most important to assess the reduction in toxicity of the waste materials and few studies have addressed this matter. For example, it is now clearly established that bacterial activities can lead to the formation of sulfoxides and sulfones (6,7,11,12). However, in only a few cases have the toxicities of these metabolites been studied.

Several questions arise from the findings of this research program and answers to these must be more fully assessed to evaluate the significance of the results to bioremediation programs. Four of these questions are:

- *Are the sulfur-containing metabolites more mobile than their parent compounds?*
- *Are the sulfur-containing metabolites formed in contaminated environments that contain a vast mixture of organic compounds and a diverse, mixed microbial population?*
- *Are the sulfur-containing metabolites resistant to further biodegradation?*
- *Are the sulfur-containing metabolites more toxic than their parent compounds?*

Current research in our laboratory is beginning to address the last three questions.

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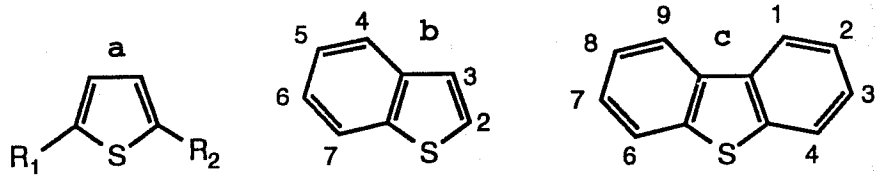

Figure 1. Compounds studied. **(a)** Alkylthiophenes: R_1 = methyl, ethyl or butyl; R_2 = *n*-alkyl (C_{13} or C_{16}) or isoprenoidal (C_{10} or C_{20}). **(b)** Benzothiophene. **(c)** Dibenzothiophene.

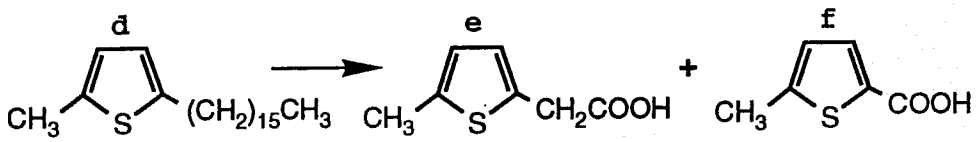

Figure 2. Metabolites of 2-hexadecyl-5-methylthiophene **(d)**. **(e)** 5-Methyl-2-thiopheneacetic acid and **(f)** 5-methyl-2-thiophenecarboxylic acid.

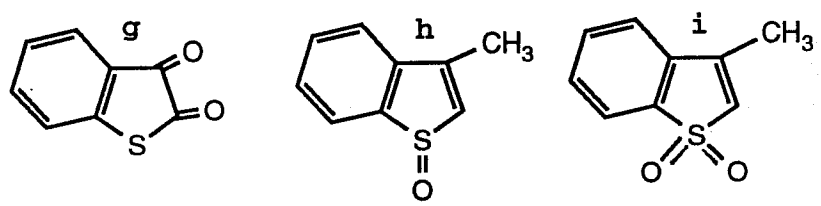

Figure 3. Metabolites produced by isolate BT1. **(g)** Benzothiophene-2,3-dione from benzothiophene. **(h)** 3-Methylbenzothiophene sulfoxide and **(i)** 3-methylbenzothiophene sulfone from 3-methylbenzothiophene.

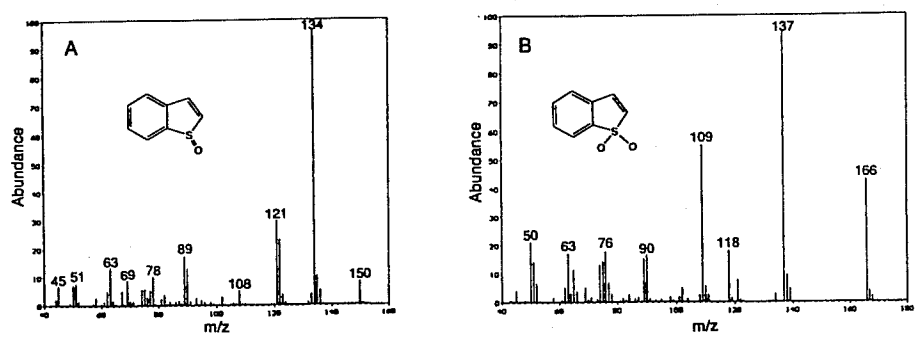

Figure 4. Mass spectra of two metabolites produced from benzothiophene by isolates W1 and F. (A) Sulfoxide. (B) Sulfone.

Table 1
Summary of the oxidized sulfur-containing metabolites produced from benzothiophene and the methylbenzothiophenes by three *Pseudomonas* isolates.

Substrate[b]	Oxidized products found in cultures of each bacterial strain[a]		
	BT1	W1	F
BT	2,3-dione	sulfoxide sulfone 2,3-dione	sulfoxide sulfone 2,3-dione
2-MBT	sulfoxide sulfone	sulfoxide sulfone	sulfoxide sulfone carboxylic acid
3-MBT	sulfoxide sulfone	sulfoxide sulfone	sulfoxide sulfone carboxylic acid methanol (?)[c]
4-MBT	2,3-dione	2,3-dione	2,3-dione
5-MBT	2,3-dione	carboxylic acid	carboxylic acid 2,3-dione
4-MBT & 6-MBT	*m*-tolyl methyl sulfoxide 2,3-diones	*m*-tolyl methyl sulfoxide 2,3-diones carboxylic acid	*m*-tolyl methyl sulfoxide 4-MBT-2,3-dione carboxylic acid
7-MBT	sulfoxide sulfone 2,3-dione	sulfoxide sulfone 2,3-dione *o*-tolyl methyl sulfoxide carboxylic acid methanol (?)	sulfoxide sulfone 2,3-dione *o*-tolyl methyl sulfoxide carboxylic acid methanol (?)

[a] None of the metabolites were found in the appropriate sterile controls. Details of the identifications are given in refs (6,13).
[b] BT = benzothiophene, MBT = methylbenzothiophene
[c] (?) = Tentatively identified, no authentic standard available

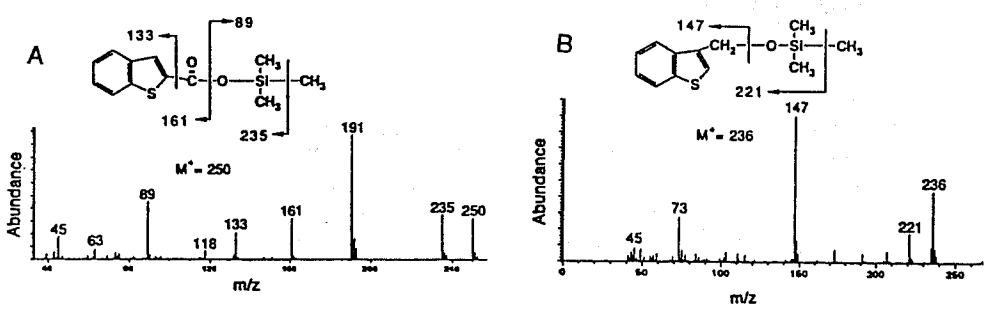

Figure 5. Mass spectra of the TMS-derivatives of two metabolites resulting from the oxidation of the methyl groups of 2-methylbenzothiophene (A) and 3-methylbenzothiophene (B).

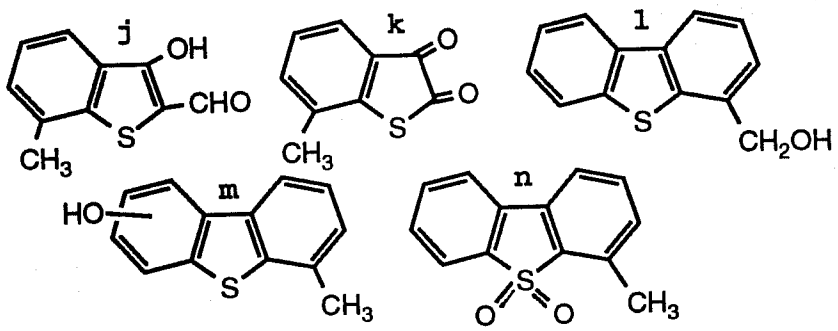

Figure 6. Metabolites produced from 4-methyldibenzothiophene by isolate W1. (**j**) 7-Methyl-3-hydroxy-2-formylbenzothiophene. (**k**) 7-Methylbenzothiophene-2,3-dione. (**l**) 4-Dibenzothiophene-methanol. (**m**) x-Hydroxy-4-methyldibenzothiophene. (**n**) 4-Methyldibenzothiophene sulfone.

Table 2

Summary of the oxidized sulfur-containing metabolites produced from methyldibenzothiophenes by three *Pseudomonas* isolates.

	Oxidized products found in cultures of each bacterial strain[a]		
Substrate[b]	BT1	W1	F
2-methyl-DBT	Me-BT-2,3-dione sulfone	Me-BT-2,3-dione Me-HFBT OH-Me-DBT DBT-methanol sulfone	Me-HFBT OH-Me-DBT DBT-methanol sulfone
3-Methyl-DBT	Me-BT-2,3-dione Me-HFBT OH-Me-DBT	Me-BT-2,3-dione Me-HFBT OH-Me-DBT	Me-HFBT
4-Methyl-DBT	Me-BT-2,3-dione Me-HFBT sulfone	Me-BT-2,3-dione Me-HFBT OH-Me-DBT DBT-methanol sulfone	Me-HFBT
1-Methyl-DBT & 3-Methyl-DBT	Me-BT-2,3-dione OH-Me-DBT	Me-BT-2,3-dione Me-HFBT OH-Me-DBT	Me-BT-2,3-dione Me-HFBT OH-Me-DBT DBT-methanol

a None of the metabolites were found in the appropriate sterile controls. Details of the identifications are given in ref (7).

b Abbreviations: DBT = dibenzothiophene; Me-BT-2,3-dione = methylbenzothiophene-2,3-dione; Me-HFBT = methyl-3-hydroxy-2-formylbenzothiophene; OH-Me-DBT = hydroxymethyldibenzothiophene.

Detection and Control of Sulfidogenesis

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Control of sulfidogenesis is important for prevention of the negative effects of sulfide production in oil and gas reservoirs and related fluid-handling facilities. Any program to control sulfide production must include monitoring of sulfide and the microorganisms primarily responsible for sulfidogenesis, the sulfate-reducing bacteria (SRB). Ideally, monitoring methods should be both simple enough for use in the field by operators and service company personnel and accurate enough for research/laboratory support. Sulfide in produced fluids must be measured in the field at the time of collection. The methylene blue assay, with either laboratory prepared reagents or test kits, reliably quantitates sulfide at the 0.1 ppm (3 nmol/ml) level. Inoculation of medium specific for SRB remains a simple way to enumerate these bacteria from fossil fuel systems. A medium has been formulated which can detect SRB with several orders of magnitude more sensitivity and in less time compared to those often used in the industry. Proper application of a biocide can control the number and activity of SRB in the fossil fuel industry.

INTRODUCTION

The negative effects of sulfidogenesis, often attributed to the activity of sulfate-reducing bacteria (SRB), in the fossil fuel industry have long been recognized (1). Control of sulfidogenesis, and of SRB, is an important concern of producers and operators in the fossil fuel industry. Biocide treatment has been a tool for the control of SRB, although it has been perceived as costly and of only qualified success. Recently, the addition of nitrate and/or sulfide-oxidizing bacteria to control sulfidogenesis was introduced (2-3). Any program designed to control sulfide production must include monitoring of both sulfide and SRB.

Sophisticated techniques have been introduced to monitor sulfide production and SRB, including the use of radiolabelled sulfate (4-5) and antibodies against components of SRB (e.g., RapidChek SRB Detection System, Conoco). Recently, DNA probes were used to monitor SRB in oil field samples and in biofilm studies (6-8). These techniques are valuable tools in the research laboratory. However, their utility for routine monitoring by operator and service company personnel in the field is less clear. The need for simple tools which can be used by personnel with little training remains.

Traditionally, SRB were monitored by enumerating viable cells from samples by most probable number (MPN). Variations of this method continue to appear in the microbiology literature (9-12). The API Recommended Practice RP 38 from the American Petroleum Institute (13) is based on MPN methodology. Recent papers on enumeration of SRB by viable cell count contain improvements in medium formulation and anaerobic technique. MPN methodology is inexpensive and can be carried out by operator and service company personnel. These techniques are useful in the laboratory, too, especially when enrichment and isolation of SRB strains from the field is desired.

Some simple assays for SRB and sulfide useful in both the laboratory and the field are described here. These assays were used to evaluate the effectiveness of a biocide to control SRB and sulfidogenesis in a biofilm device.

SULFIDE ASSAY

An assay for sulfide for use in both field and laboratory studies based on the methylene blue method (14-15) was developed. This assay may also be used to distinguish soluble and insoluble sulfides by inclusion of an initial step to remove the insoluble fraction (16).

A sulfide standard (1,000 mg/liter) was prepared as follows. Crystals of ACS reagent grade $Na_2S{\cdot}9H_2O$ (Aldrich Chemical Co., Milwaukee, WI, #20,804-3) were washed with distilled water, dried with lint-free tissue, weighed and taken into an anaerobic chamber (17).

Anoxic 0.01 N NaOH was added to give a solution containing 7.492 grams of $Na_2S \cdot 9H_2O$/liter. The standard was stored in a narrow-mouthed glass bottle sealed with a polyethylene-lined cap in an anaerobic chamber and was stable for over a year under these conditions.

The DMPD reagent for the sulfide assay was prepared by dissolving 50 ml of concentrated sulfuric acid, 1.0 gram of $Zn(CH_3COO)_2 \cdot 2H_2O$ and 1.0 gram of N,N-dimethyl-*p*-phenylenediamine·HCl (Sigma Chemical Co., St. Louis, MO, D 5129) in a liter of distilled water. The DMPD reagent was dispensed (4.9 ml/tube) into 16 x 150 mm disposable glass tubes with rubber-lined caps (Fisher Scientific, Pittsburgh, PA, 14-959-25D) and stored in the dark at room temperature. The reagent was stable for over six months. Fresh reagent is water white; reagent with a slight pink tinge should not be used for critical assays. The ferric reagent was prepared by dissolving 5.0 grams of $FeCl_3 \cdot 6H_2O$ in distilled water to a final volume of 20 ml.

The total sample volume for this assay was 5.0 ml and the final volume of each assay was 10 ml. Water was added, if required for sample volume, to an assay tube. The sulfide-containing sample was added, followed immediately by 0.1 ml of the ferric reagent and mixing. After incubation at room temperature for at least 10 minutes, the absorbance at 660 nm was measured with a Spectronic 20 (Milton Roy, Rochester, NY). Standards contained 0-5 μg or 0-10 μg of sulfide for a 19 mm or 13 mm cuvette, respectively. A standard curve for this assay is given in Figure 1. A sulfide concentration as low as 3 nmol/ml (0.1 ppm) can be measured accurately.

The assay may be performed and developed with the ferric reagent in the field, then transported back to the laboratory to measure absorbance. The developed color is stable at room temperature for at least 24 hours. High salt concentrations in brines may slightly affect the intercept point of a standard curve on the y axis (unpublished results) and should be considered during critical assays. Standard addition or other techniques may be used to compensate. The use of ammonium phosphate, indicated in some variations of the methylene blue assay (16), had no effect on the assay described here (unpublished results).

A simple one-step, inexpensive semi-quantitative assay for sulfide is commercially available which is sensitive at the 0.1 ppm level and up to the 10,000 ppm level (CHEMetrics,Calverton, VA, K-9510).

ENUMERATION OF SRB BY VIABLE COUNTS

The enumeration of SRB by serial dilution in differential medium is a simple, useful technique which requires only modest training for success. The medium described in API Recommended Practice RP 38 (13) has been a standard in the fossil fuel industry and is available from commercial sources (e.g., Williams Brothers, Tulsa, OK) for this purpose.

Since publication of the RP 38 medium in 1965 our understanding of the nutrition of SRB and other anaerobes has increased greatly (11, 18-19). A medium derived from that described in RP 38 was developed based on this understanding and compared to the RP 38 and other SRB medium for enumeration of SRB from pure cultures and environmental samples.

There are several significant differences between the derived medium, (API)-RST, and RP 38 medium (Table 1). Ammonium sulfate was included to increase the amount of ammonium and sulfate available to the SRB (the growth of many strictly anaerobic bacteria may be stimulated by elevated concentrations of ammonium, as long as pH is controlled). A calcium salt was incorporated into the (API)-RST medium. TES was used to buffer the medium; TES was found to be the best of the Good's buffers to use at near neutral pH's for the culture of bacteria (unpublished results). A trace metal solution and a water-soluble vitamin solution designed for cultivation of strictly anaerobic microorganisms (Tables 2 and 3) were included. The amount of phosphate and iron added to the medium lead to the formation of a precipitate; a precipitate may improve the recovery of SRB from environmental samples (20). Cysteine was included as a reducing agent to lower the oxidation-reduction potential of the medium to one more favorable for the recovery of SRB. The (API)-RST medium was sterilized at 121° C for five minutes. No problems were observed with medium sterility as long as new or chemically-clean glassware and reagent grade or better chemicals were used in a clean laboratory environment.

Media were prepared using strictly anaerobic technique (21-22) and dispensed into Hungate-type anaerobic culture tubes (Bellco Glass, Vineland, NJ, 2047-116125) for the media comparison studies. Media were also obtained from a commercial source (11).

Results from a comparison of media for enumeration of cells from a pure culture of SRB (11), *Desulfovibrio desulfuricans*, are summarized in Table 4. MPN values were stable after incubation at 30° C for 72 hours. The values obtained from the examined media were essentially the same, with one important exception. A commercial RP 38 medium prepared without the addition of an iron nail yielded low recoveries of SRB. The iron nail in RP 38 medium acts as a reducing agent, lowering the oxidation-reduction potential to a point more favorable for culture of SRB (23). The API Recommended Practices RP 38 (13) calls for the addition of both a ferrous salt and an iron nail to the medium; failure to include the nail would result in the enumeration of fewer viable cells.

Enumeration of cells from environmental samples was quite different from that observed with pure cultures (11). The MPN's observed from sediment collected from a leachate-contaminated aquifer (24) on different media (11) are shown in Table 5. Counts were determined after incubation at 30° C for seven days (the MPN for the (API)-RST medium was stable for 23 days past that time). SRB were not recovered on any the RP 38 media examined after seven days of incubation. These and

other results (11) demonstrate the deficiency of RP 38 medium for detection and enumeration of SRB from environmental samples.

Final MPN's could be determined from (API)-RST medium after 15 days of incubation compared to the 30 days often recommended for enumeration of SRB (11, unpublished results). (API)-RST medium can be adapted for enumeration of other SRB by alteration of carbon and energy sources and other simple manipulations. This medium was used in several recent microbial ecology studies (25-27).

CONTROL OF SRB/SULFIDOGENESIS

A study was conducted to determine the most effective biocide dosing regime (concentration of biocide, duration of biocide dose and interval between biocide doses) using the methods described above (28). Low volume, circulating test loops for biofilm development and monitoring were constructed from mild steel using a design adapted from the brass Robbins device (29). Test loops were subjected to a high biofouling pressure; each minute 10 mls of an entry water were pumped into each 300 ml test loop. This entry water contained, per ml, 3 mg of trypticase soy broth, 8 mg of sodium lactate, 5 x 10^7 SRB and 1.2 μg sulfide (1.2 ppm sulfide) (28). A biocide (a mixture of 5-chloro-2-methylisothiazol-3-one and 2-methylisothiazol-3-one) was metered into circulating test loops for 12 hours each day at the concentration shown in Table 6.

Formation of a SRB biofilm and sulfidogenesis under this high biofouling pressure was controlled for at least 15 days, provided that a sufficient concentration of biocide was applied (Table 6). It should be noted that the concentration of sulfide in the effluent of the circulating test loops treated with 6 ppm of biocide at day 15 (0.4 ppm) was less than that entering the test loops (1.2 ppm). These results suggest that proper application of biocide can control the number and activity of SRB in above ground water handling systems in the fossil fuel industry and, probably, other circumstances.

The need for simple techniques to monitor SRB and sulfide production still exists in the fossil fuel industry. The techniques described above have proved useful in the field, in the author's laboratory and in the laboratories of other investigators and can meet the monitoring needs of operators and service companies in this industry.

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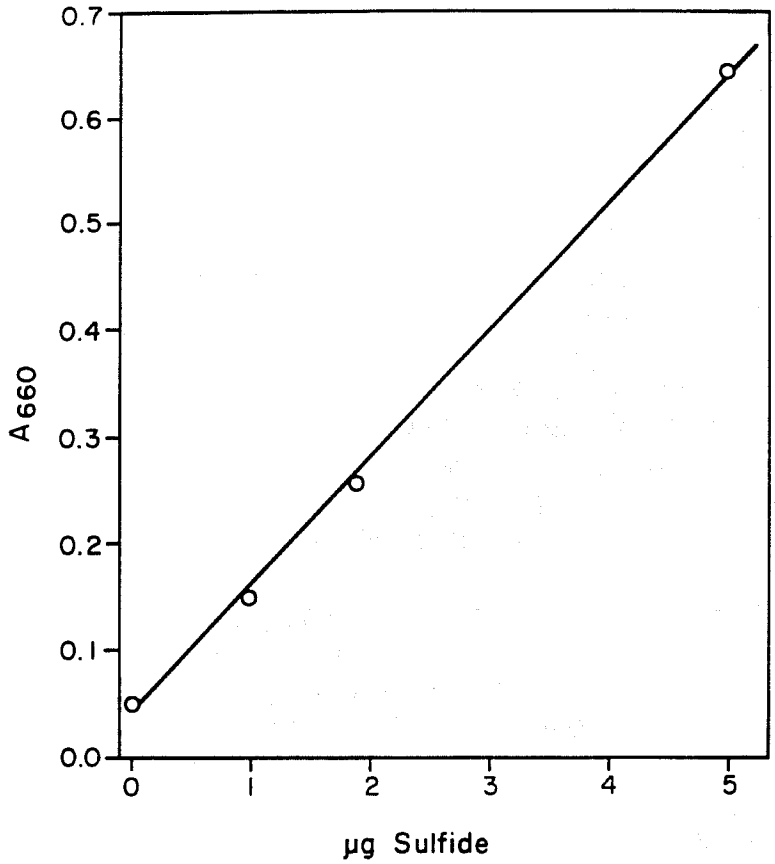

Figure 1. A standard curve for the modified methylene blue sulfide assay.

Table 1.
Composition (grams/liter) of RP 38 and (API)-RST Media for Enumeration of SRB.

Component	(API)-RST	RP 38
Sodium lactate	4.2	2.4
Yeast extract	0.7	1
NaCl	10	10
$(NH_4)_2SO_4$	0.3	
K_2HPO_4	0.6	0.01
$MgSO_4 \cdot 7H_2O$	0.2	0.2
$CaSO_4$	0.04	
TES	1.5	
Vitamin solution	10 ml	
Trace metal solution	5 ml	
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.3	0.2
Iron nail		+
Ascorbic acid	0.1	0.1
Cysteine·HCl	0.2	

Table 2.
Vitamin Solution

Component	mg/Liter
Pyridoxine·HCl	10
Thiamine·HCl	5
Riboflavin	5
Calcium pantothenate	5
p-Aminobenzoic acid	5
Nicotinic acid	5
Thioctic acid	5
Vitamin B_{12}	5
Biotin	2
Folic acid	2
MESA[a]	10

[a]Mercaptoethanesulfonic acid.

Table 3.
Trace Metal Solution

Component	Grams/Liter
Nitrilotriacetic acid adjust pH to 6 with KOH	2.0
$MnSO_4 \cdot H_2O$	1.0
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.8
$CoCl_2 \cdot 6H_2O$	0.2
$ZnSO_4 \cdot 7H_2O$	0.2
$CuCl_2 \cdot 2H_2O$	0.02
$NiCl_2 \cdot 6H_2O$	0.02
$Na_2MoO_4 \cdot 2H_2O$	0.02
Na_2SeO_4	0.02
Na_2WO_4	0.02

Table 4.

Effect of Medium on Enumeration of *Desulfovibrio desulfuricans*.

Medium	MPN/ml[a]
(API)-RST	8×10^7
RP 38	7×10^7
Postgate's B	7×10^7
RP 38, commercial	2×10^8
RP 38, commercial, -Fe°	2×10^1

[a]MPN determined after incubation for 72 hours at 30° C.

Table 5.

Effect of Medium on Enumeration of SRB from an Aquifer Sediment.

Medium	MPN/ml[a]
(API)-RST	3×10^3
RP 38	$<2 \times 10^0$
Postgate's B	4×10^2
RP 38, commercial	$<2 \times 10^0$
RP 38, commercial, -Fe°	$<2 \times 10^0$

[a]MPN determined after seven days of incubation at 30° C.

Table 6.

Effect of Biocide on SRB in a Biofilm and Sulfide Production in a Mild Steel Flow System.

Biocide[a]	Day 8		Day 15	
mg/ml	SRB/cm^2	Sulfide mg/liter	SRB/cm^2	Sulfide mg/liter
0	1×10^8	7.0	1×10^7	13
2	2×10^1	0.1	2×10^7	10
6	2×10^2	>0.1	2×10^2	0.4

[a]5-Chloro-2-methylisothiazol-3-one and 2-methylisothiazol-3-one dosed 12 hours/day.

Microbial Treatment of Sour Produced Water

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ABSTRACT

The potential for detoxification and deodorization of sour produced waters by microbial treatment was evaluated under field conditions. A sulfide-tolerant strain of the chemautotroph and facultative anaerobe, *Thiobacillus denitrificans*, was introduced into an oil-skimming pit of the Amoco Production Company LACT 10 Unit of the Salt Creek Field, WY. Field-produced water enters this pit from the oil/water separation treatment train at an average flowrate of 5,000 bbl/d (795 m^3/d) with a potential maximum of 98,000 bbl/d (15,580 m^3/d). Water conditions at the pit inlet were 4,800 mg/L TDS, 100 mg/L sulfide, pH 7.8, and 41.7°C. An aqueous solution of ammonium nitrate and diphosphorous pentoxide was added to this water to provide required nutrients for the bacteria. The first 20% of the pit was aerated to a maximum depth of 5 ft (1.5 m) to facilitate the aerobic oxidation of sulfide. No provisions for pH control or biomass recovery and recycle were made.

Pilot operations were initiated in October 1992 with the inoculation of the 19,000 barrel (3,020 m^3) pit with 40 lb (18.1 kg) of dry weight biomass. After a brief acclimation period, a nearly constant mass flux of 175 lb/d (80 kg/d) sulfide was established to the pit. Bio-oxidation of sulfide to elemental sulfur and sulfate was immediate and complete. Subsequent pilot operations focused upon process optimization and process sensitivity to system upsets. The process appeared most sensitive to large variations in sulfide loading due to maximum water discharge events. However, recoveries from such events could be accomplished within hours.

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INTRODUCTION

Water or brine co-produced with petroleum is often contaminated with soluble inorganic sulfides (H_2S, HS^-, S^{-2}) which result from the activity of sulfate-reducing bacteria or other sulfide-producing bacteria in the reservoir and well bore. These sulfides can make a significant contribution to the toxicity of these brines and must frequently be removed prior to surface discharge. A common method of treating these brines is to air strip the sulfides as H_2S. However, this method of "treatment" simply converts a potential water pollution problem into an air pollution and odor problem.

The ability of the chemoautotroph and facultative anaerobe *Thiobacillus denitrificans* to deodorize and detoxify an oil-field produced water containing sulfides was previously evaluated under simulated field conditions (1). A sulfide-tolerant strain of *T. denitrificans* (strain F) was used to remove inorganic sulfide from a synthetic sour brine containing 4000 mg/L total dissolved solids (TDS) and 100 mg/L sulfide (2). The sour brine was treated continuously in a rectangular plugflow reactor which approximated the scaled dimensions of an existing field detention pond. The head space of the reactor was purged with N_2 in order to capture H_2S off-gases in a zinc acetate trap. Brine was fed to the reactor continuously for 90 days at rates corresponding to residence times of 0.17-6 days. Temperature and pH ranged from 22-40.5°C and 7.5 - 8.8, respectively. The start-up biomass concentration was approximately 100 mg/L (by dry weight). No additional *T. denitrificans* biomass was added to the reactor after start-up. At residence times of 0.3 days and greater inorganic sulfide was undetectable in the effluent. H_2S was not detected in the outlet gas or the zinc acetate trap. Approximately 80% of the sulfide feed was oxidized to sulfate and removed from the reactor in the liquid effluent. The remainder was partially oxidized to elemental sulfur which was retained in the reactor. These experiments demonstrated that oxidation of inorganic sulfides by *T. denitrificans* represents a viable process concept for the treatment of sour water co-produced with oil and gas.

This process of microbial oxidation of sulfides in sour produced water has now been field tested at Amoco Production Co. Salt Creek Field in Midwest, Wyoming. The Salt Creek Field is located 40 miles north of Casper, WY, and is one of the oldest oil fields in the region. Currently, it is operated as a mature water flood with approximately 1,000 production and 950 injection wells. Production averages 10,000 barrels (1590 m^3) of oil and 750,000 (119,250 m^3) barrels of water per day. Of the total water production nearly 95% is reinjected while the remainder is discharged to the surface. These discharges are termed "beneficial" in that they represent an important source of fresh water for the support of local livestock and wildlife in this predominantly arid region.

Over time, produced fluids from the field have become progressively sour due to microbial reduction of sulfate introduced into the reservoir during water flooding. Because potential odor and toxicity issues are associated with sour water discharges, the merits of this practice are under active evaluation (3). If complete water reinjection is to be avoided, a cost-effective treatment option which allows the continued discharge of water while eliminating the odor and toxicity attributed to H_2S must be found.

Several remediation options exist for the control of soluble inorganic sulfides in water such as chemical oxidation, air stripping, precipitation, air oxidation, and biological treatment to name a few. For Salt Creek, the choice of a particular treatment option is severely restricted by the operating environment. Beyond obvious technical issues, the most significant restrictions are associated with stringent capital and operating expense limits. Of necessity these limits mandate the use of existing facilities (production pits) and manpower. Of the accepted chemical or physical treatment options available, most can be rejected because of their high operating expenses, capital costs, or inability to effect immediate H_2S odor control in an unconfined production pit. Only biological treatment appears to offer sufficient process flexibility to achieve effective control at low costs and under the imposed operating restrictions. The method chosen was bioaugmentation of existing pits and lagoons of the Salt Creek discharge system with a self-sustaining bacterial population capable of efficient sulfide oxidation at prevailing conditions, specifically, *T. denitrificans* (strain F).

SITE DESCRIPTION

The LACT 10 unit of the Salt Creek Field is an oil/water separation facility wherein approximately 1,000 bbl/d (159 m^3/d) oil and 98,000 bbl/d (15,580 m^3/d) water are processed. Upon separation, water is diverted from the treatment train to a large transfer tank from which all but 5,000 bbl/d (795 m^3/d) is routinely utilized for water flood reinjection. The 5,000 bbl/d overflow is shunted to the surface discharge system in order to maintain the associate pits, lagoons, and wetlands. On occasion, injection plant failures necessitate full discharge to the surface system. Thus, large flowrate variations are inherent to the system.

Water enters the surface discharge system at Pit 1 through a submerged 40 cm line. Pit 1 is an earthen lagoon which serves as an oil-skimming pond. It's approximate dimensions are 79 m x 34 m with a variable depth from 0.3 - 6 m The estimated volume of the pit is 19,000 bbl (3020 m^3). From Pit 1 water flows to a series of smaller detention pits, over a cascade, through a meandering lagoon, and eventually to Salt Creek.

The average water temperature entering Pit 1 is 107°F and the pH is slightly alkaline (7.8). The brine is relatively fresh with a Total Dissolved Solids (TDS) content of 4,800 mg/L. The brine composition is reported in Table 1. The sulfide concentration is 100 mg/L. Based on an average daily flowrate of 5,000 bbl (795 m^3), sulfide influx to the pit is about 80 kg/d. Dissolved oxygen (DO) levels within the pit are less than 1 mg/L; the pit is largely anoxic.

PILOT DESIGN/OPERATION

Pit 1 was chosen as the primary treatment facility for the bioaugmentation pilot because of capital limitations, . Conceptually, the piloting program sought to establish the efficacy of "seeding" Pit 1 with a self-sustaining population of *Thiobacillus denitrificans* strain F capable of sulfide oxidation under prevailing conditions of flowrate, temperature and sulfide flux. Contrary to the laboratory prototype, the facility was designed as a partially aerated basin to facilitate mixing and to take advantage of higher reaction rates associated with the aerobic bio-oxidation of sulfide. The collection and recycle of biomass

from pit effluents was not attempted because of the extensive facilities modifications required. Carbon for cell growth was obtained from the field brine as carbonate (Table 1). Additional nutrients were limited to ammonia added as ammonium nitrate and phosphate as P_2O_5.

CONSTRUCTION

Two modifications to the existing LACT 10 facility were required to conduct the pilot; specifically, the means to add nutrients to the discharge water prior to its entering the pit and aeration of approximately one-fourth the pit volume.

Because of cost and availability, the primary nutrient and electron acceptor source, ammonium nitrate, was obtained as a prilled solid in 18.2 kg bags. This necessitated the construction of a batch-mixing facility to deliver the nutrient in liquid form. The mixing facility consisted of two 2.8 m^3 fiberglass tanks each outfitted with a centrifugal pump for solids circulation. The first tank served as a primary mixing tank. The second tank served as a holding and delivery vessel. Nutrient solution was metered to the produced water discharge line by means of a variable stroke chemical metering pump. All materials used in the construction of the system were compatible with corrosive liquids. The entire mixing facility was enclosed within an earthen berm for spill containment. Drainage was provided to the pit.

An air manifold was constructed and connected to an existing 1,000 SCFM (28 std m^3/min) blower (Sutorbilt 7 MF) to completely aerate the first thirty feet of the pit. The manifold was made from 12.7 cm PVC pipe and extended down either side of the pit. PVC laterals 7.6 cm in diameter were spaced at 1.5 m intervals on each leg of the manifold. The laterals were 18.3 m in length. Holes (0.64 cm) spaced on 0.3 m centers were drilled in the last 9.1 m of each capped lateral. To provide aeration at depth, the laterals were weighted with several 6.1 m lengths of 1.3 cm iron rod. The approximate average depth of aeration was 1.5 m. A valve was placed on each lateral to control and balance air rates.

With the exception of the aeration manifold, all major capital items were obtained from field surplus equipment. Field personel were utilized for construction at an estimated cost of material and labor of $5,000.

PILOT START-UP

A sufficient amount of biomass had to be cultured in order to adequately "seed" the pit prior to physically operating the pilot. About 18 kg (dry weight) of flocculated *T. denitrificans* strain F was produced as previously described (4) and shipped to the site in 55-gal drums.

Actual pilot operations began on October 21, 1992. A complete physical and chemical survey of the pit was conducted before inoculating the pit. Direct nutrient addition to the discharge was initiated approximately 36 hours before inoculation. The nutrient was added as a 40 wt% ammonium nitrate concentrate supplemented with 0.16 lb/gal (0.019 kg/L) P_2O_5. Both chemicals were obtained from a commercial source (Jirdon Agri Chem, Torrance, WY) and

were made-up in the field produced water. Initial nutrient rates were based upon the calculated nitrate requirement (3.29 mg NO_3-/mg S^{-2}) to achieve complete sulfide oxidation under anoxic conditions for an average daily influx of sulfide (1). At this rate biomass requirements for nutrient nitrogen (0.084 mg NH_3/mg S^{-2}) and phosphorous (0.013 mg PO_4^{-3}/mg S^{-2}) were easily attained (5).

A method was devised to reduce the influx of sulfide to Pit 1 during start-up. The discharge flowrate was lowered from 5,000 (795 m^3/d) to 1,000 bbl/d (159 m^3/d) and the water was stripped with air upstream of Pit 1 to reduce the sulfide concentration from 100 mg/L to nearly 10 mg/L. In so doing, the potential to overload the small inoculum and thereby exceed its toxicity limit to sulfide was diminished significantly. The pit was inoculated on October 24 by pouring the biomass concentrate directly into the pit near the discharge inlet. The presence of adequate nutrients at the point of inoculation was insured by the direct addition of fertilizers to the inoculation area.

OPERATION

The pilot was operated continuously from October 21, 1992 to April 10, 1993. The first three days post inoculation served as an acclimation period for the bacteria. The sulfide flux to the pit was kept low by air stripping during this period. On Day 9 (elapsed time from 10/21) the water discharge rate was returned to its daily average of 5,000 bbl (795 m^3). As a consequence, the sulfide influx to the pit increased although stripping continued. From Day 9 to Day 14 air was gradually diverted from the stripper to the pit aeration system. By Day 14, 100% of the blower capacity [950 CFM (26.9 m^3/min) @ 10 psig] had been diverted to the pit. At this point the sulfide flux to the pit was approximately 92 kg/d. Flow and air rates remained constant thereafter, unless otherwise noted.

On Day 17 nutrient influx to the pit was reduced from its start-up level to a level based upon twice the calculated ammonia demand. This was done to determine if nitrate was required in lieu of oxygen for anoxic oxidation of sulfide. Further reductions in the nutrient rate were attempted throughout the program to assess the minimum nutrient requirement.

Several instances of operational upsets were of note. On three separate occasions (Days 43, 100, and 135) full discharge events occurred. These events were initiated by unforeseen injection plant failures of variable duration. The longest was on Day 135 and lasted for nearly two days. During these periods no attempt was made to adjust nutrient delivery rates in accordance with the flowrate. Hence, sulfide fluxes to the pit exceed anticipated nutrient requirements. In an related instance (Day 34), water flow to the pit fell significantly below the daily average due to a controller failure. Because this event occurred while ambient temperatures were significantly below freezing, pit temperatures briefly dropped below stated optimums for bacterial activity. On numerous other occasions, pump, aerator, or pipe ruptures interrupted air or nutrient service to the pit. Typically, these events were of short duration and negligible effect.

MONITORING

An intensive monitoring program to assess pilot performance was undertaken during the first weeks of start-up and operation . Key variables included aqueous phase sulfide, nitrate, phosphate, ammonia, sulfate, and dissolved oxygen concentrations. Flowrate, pH, and temperature were also monitored. Sampling of the discharge system routinely occurred at three locations: (1) upstream of Pit 1, (2) from Pit 1 at the influent position and, (3) the effluent from Pit 1. Periodically, additional samples were obtained elsewhere within the pit and the discharge system. Nutrient delivery rates were estimated by gauging the nutrient holding tank daily.

Most water analyses were conducted by spectral methods with a Hach DR/2000 spectrophotometer. These included Nessler ammonia, nitrate by cadmium reduction, sulfate by barium precipitation, and reactive phosphate. Reagents were obtained from Hach Chemical Company (Loveland, CO) with a stated accuracy supplied by the manufacturer. Sulfide ion was determined by Sensidyne Gastec sulfide ion analyzer tubes. The stated accuracy was ±2 ppm over a 0 to 100 ppm range. The pH and temperature were determined with a Beckman Φ11 portable pH meter. A two point calibration procedure was performed routinely. Dissolved oxygen was measured with Chemetric (Calverton, VA) test kits for low (0-1 ppm) and high (0-10 ppm) ranges. All tests were conducted in the field within minutes to hours of sampling.

Ambient air quality above the pit surface was monitored periodically with an Industrial Scientific HMX 271 personal air monitor. The detection limit of the instrument is less than 1 ppm. The stated accuracy is ±2 ppm. The instrument was calibrated daily with a known H_2S/N_2 gas mixture standard.

Water flowrates were estimated by timing the water discharge into a container and averaging several determinations. The method proved effective for rates below 10,000 bbl/d (1590 m^3/d). For rates above this value, estimates were calculated on the basis of the difference between daily injection plant volumes and monthly total water production averages. Estimates based on this method are subject to significant error.

Water samples for bacterial enumerations were obtained at preinoculation (Day 0), post inoculation (Day 4), Day 17, 48, and 50. Enumerations were based on the most probable number (MPN) method using thiosulfate as the sole energy source (6). Hence, MPN determinations were specific to sulfur-oxidizing bacteria.

Daily monitoring occurred from Day 0 to Day 35 and from Day 49 to Day 56. Otherwise, pilot data were collected by field personnel as time allowed. Only routine analyses (sulfide, nutrient rate, and flowrate) were attempted at these times, although periodic ammonia, pH and temperature data were also collected.

RESULTS AND DISCUSSION

Prior to inoculation and nutrient addition, a background survey of Pit 1 and the associated discharge system was conducted to determine sulfide losses under prepilot conditions. Specific analytes included sulfide, dissolved oxygen,

ammonia, and nitrate in addition to temperature and pH. At the time of the survey the air stripper was operating and the flowrate to the discharge system was 3,500 bbl/d. Pit 1 was partially aerated.

On the basis of survey data, it was reasonably established that prior to inoculation no significant reduction of sulfide occurred within the pit at residence times on the order of days. Specifically, upstream of the air stripper water conditions were 100 mg/L, sulfide, 41.7°C, and pH 7.3. After the stripper, water entered Pit 1 at 28 mg/L sulfide, 32.2°C, and pH 7.8. Pit 1 effluent was 28 mg/L, 27.2°C, and pH 8.4. A significant loss of sulfide was associated with stripping but little, if any, with passive volatilization and oxidation within Pit 1. The latter was in spite of a calculated five-day hydraulic residence time. The absence of sulfide losses within the pit were potentially attributed to (1) a hydraulic short-circuit which significantly reduced fluid residence times, or (2) a shift to higher pH values and concomitantly a propensity for dissolved hydrogen sulfide to remain in solution as bisulfide ion. The temperature survey at the pit periphery did to indicate a hydraulic short-circuit since cold spots or stagnant regions were not identified. The pH data, however, did confirm a shift to higher pH values and presumably higher sulfide solubilities. Higher pH values were likely a consequence of contact between the discharge water and the alkaline soils of the pit.

Initial dissolved oxygen (DO) levels within the pit were uniformly less than 1 mg/L with minimal aeration. Ammonia and nitrate concentrations were also very low prior to nutrient addition. Hence, the need for aeration and nutrient addition were confirmed.

Sulfide concentrations at the point of discharge to the pit (within the aerated zone) and in the effluent are reported versus elapsed operating time in Figure 1. As was mentioned previously, sulfide influx to the pit was limited by air stripping prior to and immediately after (Day 4 - Day 16) inoculation with *T. denitrificans*. During this acclimation period the sulfide influx to the pit was gradually increased from 0 to the typical daily average of 80 - 100 kg/d. The corresponding sulfide concentrations over this time span never exceeded 5 mg/L at the inlet. Moreover, no sulfide was detected in Pit 1 effluents. Hence, it appeared that the bacteria were capable of oxidizing average sulfide loads to the pit within a matter of days post inoculation and the cessation of stripping.

After acclimation, pit effluent sulfide concentrations remained zero but for three upset events. On a cumulative basis this performance represented a treatment efficiency approaching 99% of the total sulfide discharged to the surface system. (In the absence of upsets this treatment efficiency approached 100%.) Under normal operating conditions, the oxidation of sulfide to sulfate appeared complete. For instance, during one three-day period the average concentration of sulfide entering the pit was 110 mg/L, while the net sulfate concentration exiting the pit was 340 mg/L. This value agrees well with the expected mass ratio of sulfate to sulfide of 3 to 1, if oxidation is complete.

With respect to fugitive emissions, H_2S was not detected immediately above the pit surface under normal operations. This was a consequence of the ability of the bacteria to instantaneously oxidize sulfides as they entered the pit; evidence of which was demonstrated by near inlet samples whose sulfide content rarely exceeded 5 mg/L. In terms of treatment efficiency, this performance

represented a minimum of 95% sulfide removal within the first few feet of the aerated zone of the treatment system.

Significant discharges of sulfide from the pit occurred as upset events on Days 34, 46, 110, and 136. They could be attributed to two causes. The first (Day 34) was unique in that low flowrates to the pit and low ambient temperatures (<-18°C) combined to cause water temperatures within the pit to drop below 15.6°C. At this temperature biological sulfide oxidation was significantly inhibited to the extent that an upset was observed. The upset was quickly remedied, however, by raising the flowrate to the pit to maintain water temperatures closer to the optimum of 30°C. The second cause for pilot upsets was largely uncontrollable. On Days 46, 110 and 136 sulfide influx to the pit significantly exceeded the daily average, i.e., >500 vs. 90 kg/d. These occurrences were caused by injection plant failures which necessitated full discharge to the pit (see Figure 2). Each was characterized by a large sulfide flux, rapid temperature increase, and inadequate nutrient supply imposed by the unanticipated large hydraulic throughput. The pilot response to these failures was encouraging in that approximately 30% of the total sulfide was at least partially oxidized. Partial oxidation was observed as an accumulation of elemental sulfur on the banks of the pit and the absence of sulfate ion in pit effluents. In terms of sulfide removal, recovery from these events was evidenced in a matter of hours of the flow returning to normal. However, complete stoichiometry oxidation of sulfide to sulfate (mass of sulfate = 3 x mass sulfide) required several days for recovery. The observation that *T. denitrificans* resorted to a partial oxidation of sulfide under stress was in keeping with laboratory observations of similar events (5,7). Moreover, the production of elemental sulfur served as a convenient visual indicator of a stressed treatment system.

Because the addition of nitrate as an alternate electron acceptor represented the largest chemical demand for the pilot, the requirement for nitrate was assessed within days of inoculation. This was accomplished by gradually reducing the nutrient rate to the pit over a period of several days to a lower limit based upon the calculated ammonia requirement (0.084 kg NH_3/kg S^{-2}). By Day 14 the nitrate influx to the pit dropped below the calculated nitrate demand (3.29 kg NO_3-/kg S^{-2} times the sulfate mass flowrate in kg/D) and, thereafter, always remained below it. At no time could a pilot upset be attributed to this condition. Therefore, it was presumed that the biological oxidation of sulfide occurred in large measure aerobically. This conclusion was based upon the fact that oxidation of sulfide by denitrifying mechanisms is not instituted in *T. denitrificans* until O_2 levels fall below 1 mg/L.

Ammonia influx to the pilot remained for the most part above the calculated demand. Overall, it would appear that the calculated ammonia demand was sufficient to sustain the bacterial population in the pit with an adequate margin of safety.

Generally, the pH of the influent to Pit 1 ranged from 7.0 to 8.0 in the absence of air stripping. After microbial treatment, however, the pH of the discharge water was more alkaline (8.0-8.6) with no discernible difference from entrance to exit. The relatively low pH of the upstream fluids was consistent with the amount of dissolved H_2S in the water. Although complete oxidation of sulfide was indicated, the excess acidity associated with sulfuric acid production

was apparently removed by contact with the alkaline soils of the pit. At no time did the pH within the treatment system appear to affect sulfide oxidation by *T. denitrificans*.

Under normal flow conditions the pit temperature averaged about 23.9°C with a maximum day-to-day fluctuation of about 5.6°C. Fluctuations were attributed to changes in flowrate or heat input to the pit and variable ambient temperatures. (Over the piloting period ambient temperatures ranged from -23.3 to 23.9°C). During full discharge events, large temperature increases were realized within the pit in a matter of hours. On one such occasion the observed change was -1.8°C. Fortunately, such temperature swings had no discernible lasting effect on pilot performance.

Bacterial enumerations by the MPN method are reported in Table 2. These enumerations were specific to bacteria capable of utilizing reduced sulfur as their sole energy source. Enumerations were conducted before pit inoculation, 15 minutes and two days afterwards, and on Days 17, 48, and 50. All water samples for bacterial counts were obtained adjacent to the discharge point to Pit 1. The background bacterial count was $4.5x10^3$/mL, most of which were identified as aerobic organisms incapable of utilizing nitrate for anaerobic sulfide oxidation. Immediately after inoculation the bacterial count increased to $4.5x10^7$/mL. These bacteria were capable of using nitrate and thus indicated that viable *T. denitrificans* had been introduced to the pit. Subsequent bacterial enumerations were on the order of 10^7/mL and the bacteria were always capable of nitrate utilization. This suggested that a steady state population of *T. denitrificans* had been established. Whether indigenous organisms were significantly represented in this population is unknown.

Finally, the primary expenses associated with pilot operations were nutrient costs and energy costs for aeration. With respect to nutrient utilization, a minimum demand based upon ammonia requirements appears to offer a reasonable lower limit. Using ammonium nitrate as the ammonia source at a cost of $0.22/kg, the estimated chemical treatment cost for the LACT 10 discharge is $0.0014/bbl ($0.0089/m^3). The rated horsepower of the blower at 1640 RPM and 10 psig backpressure is 58. The calculated energy cost per day at $0.03/kW-hr is $31.10. For an average daily flow of 5,000 bbl/d (795 m^3/d), the energy cost per treated barrel is $.0062. The total treatment cost is thus approximately $0.0076/bbl ($0.048/m^3) or about $38/d. Contrary to operating expenses, maintenance costs were rather high. This was attributed to repeated materials failures during cold weather and in the presence of corrosive nutrient solution.

CONCLUSIONS

This work demonstrates the successful application of a bioaugmentation technology for the treatment of hydrogen sulfide laden produced water discharges to control fugitive air emissions from said discharges. Specifically, the following was demonstrated:

1. *Thiobacillus denitrificans* was successfully introduced into the existing discharge system of the LACT 10 unit of the Salt Creek Field, WY.

2. Sulfide removal efficiencies approaching 99% could be attained for routine discharges of 5,000 bbl/d (795 m^3/d) containing 100 mg/L sulfide.

3. Aerobic sulfide oxidation to sulfate was almost instantaneous and no odorous emissions of H_2S were detected emanating from the discharge under normal conditions.

4. As designed and operated, the system was capable of processing about 10,000 bbl/d (1590 m^3/d) or 160 kg S/d.

5. Pilot recovery from transient full discharge upset events (98,000 bbl/d or 15,580 m^3/d) was on the order of hours. Partial oxidation of sulfide to elemental sulfur was indicated during such events.

6. Minimum nutrient requirements were based upon bacterial reduced nitrogen (NH_3) needs. A requirement for nitrate as an alternate electron acceptor for anaerobic oxidation of sulfide was not demonstrated.

7. A steady state population of *T. denitrificans* was established at about 10^7/mL without provisions for biomass recycling. This population was stable even in the event of full hydraulic discharges.

8. Estimate treatment costs for normal discharges were less than 1 cent per barrel.

ACKNOWLEDGMENTS

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Table 1

Composition of Salt Creek Discharge Brine

Component	g/L
$CaCl_2 \cdot 2H_2O$	1.33
$MgSO_4 \cdot 7H_2O$	1.32
$MgCl_2 \cdot 6H_2O$	0.23
KCl	0.018
$Na_2CO_3 \cdot H_2O$	0.086
$NaHCO_3$	1.15
NaCl	1.82
Total Dissolved Solids (TDS)	4.81
pH = 8.5	

Table 2

Bacterial Enumerations of Sulfide Oxidizers by MPN Method

Day	Bacteria/mL	NO_3 - Utilization
3	1.5×10^7	Yes
17	9.5×10^7	Yes
48	7.5×10^7	Yes
50	2.5×10^7	Yes

FIGURE CAPTIONS

Figure 1
Sulfide concentration in the influent to Pit 1 and in the inlet and effluent ends of Pit 1.

Figure 2
Hydraulic flowrate to Pit 1.

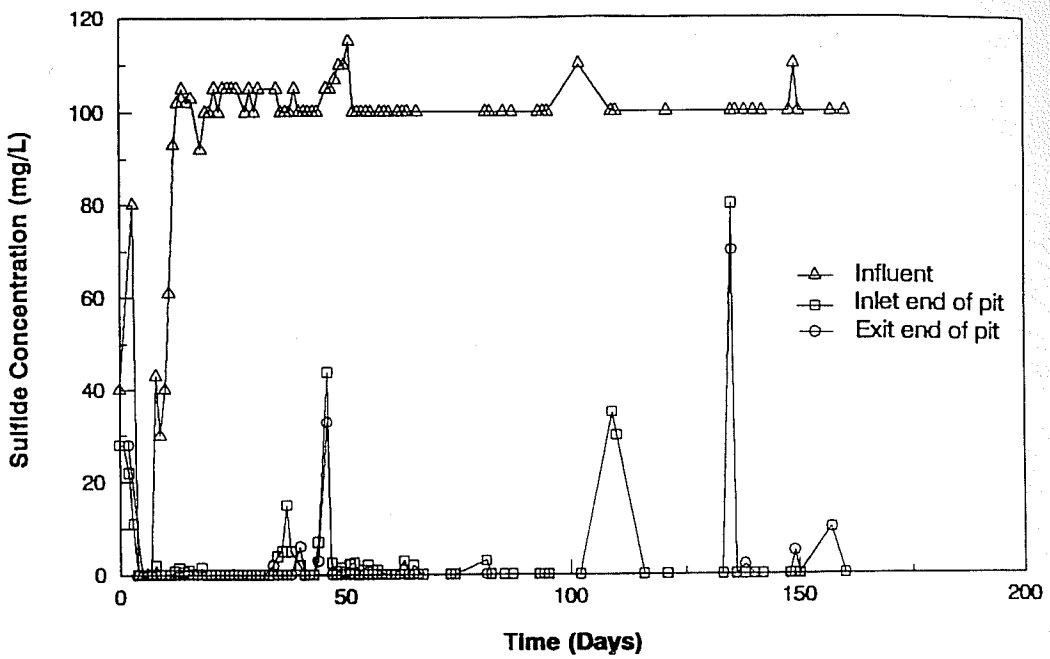

Figure 1
Sulfide concentration in the influent to Pit 1 and in the inlet and effluent ends of Pit 1.

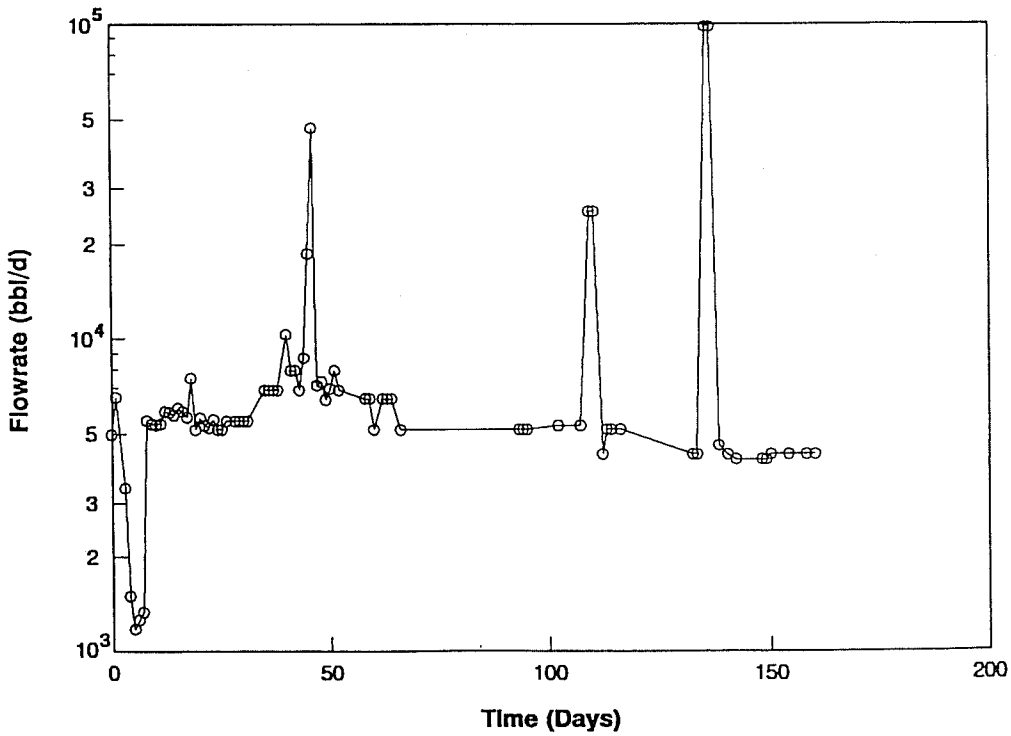

Figure 2
Hydraulic flowrate to Pit 1.

Control of Souring by a Sulfide-Resistant Strain of *Thiobacillus denitrificans*

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A microbial process to remove H_2S from gas streams has been developed. The concentration of sulfide in the liquid medium was very low, about 1 μM, resulting in very low effluent H_2S concentrations, when *Thiobacillus denitrificans* was grown aerobically or anaerobically, in batch or continuous culture, under sulfide-limiting conditions. A sulfide- and glutaraldehyde-resistant strain of *T. denitrificans* (strain F) immobilized with heterotrophic floc-forming bacteria successfully treated sour water containing 25 mM soluble sulfides. Strain F prevented the accumulation of sulfide by sulfate-reducing bacteria, in both liquid culture and sandstone cores. Strain F was effective in reducing sulfide concentrations in an experimental system of cores and formation water from a natural gas storage facility. Strain F was more effective than indigenous nitrate-using bacteria in the control of sulfide production by sulfate-reducing bacteria in a porous rock biofilm. Strain F was present and remained metabolically active in the core system for a period of 8 months. These studies show that microbial control of souring is effective, and technically simple in its application.

In marine environments, estuaries, and petroleum reservoirs, sulfate is in high concentration, and the oxidation of organic matter to carbon dioxide is coupled to the reduction of sulfate to sulfide by sulfate-reducing bacteria (SRB) (1-3). SRB are strictly anaerobic bacteria that are found in virtually any anaerobic environment conducive to microbial growth (1). These organisms use a wide range of organic compounds, and H_2 to reduce sulfate, other oxyanions of sulfur, and elemental sulfur to sulfide (1,2). The electrons donors used for these processes are end-products of the metabolism of fermentative heterotrophs, and are readily available in the consortium of bacteria found in anaerobic environments. Sulfate reducers were thought to be the only organisms found in oil/gas reservoirs that produce sulfide. However, recent studies showed that the most commonly detected sulfide-producing bacteria, such as *Shewanella putrefaciens*, do not use sulfate as an electron acceptor, but use other sulfur oxyanions (4). Thus, the number of bacterial groups of bacteria involved in sulfide production in anaerobic environments is much greater than previously thought.

Microbial sulfide production is directly or indirectly responsible for major damage to facilities in the petroleum industry each year due to the corrosion of tanks, pipelines, valves, pumps, etc. (5). Microbial sulfide production also leads to the souring of natural gas and crude oil, where the sulfur content of the fossil fuel is increased, which decreases its value, and increases transportation and refining costs. The control of microbial sulfide production is important for the economical exploitation of these fossil resources. The most common approach is to inhibit sulfide production by inhibiting the growth of SRB. For example, in the secondary production of petroleum, water used in the flooding operations is treated with a biocide (typically glutaraldehyde) to kill or inhibit the growth of SRB in the injection well, reservoir, and surface facilities. Because SRB are strict anaerobes, aeration of flooding waters can also be used to inhibit sulfide production. These measures are often of limited effectiveness since SRB are attached to solid surfaces, entrapped with other bacteria in polysaccharide-coated biofilms. Within these biofilms, the SRB find themselves in a somewhat protected environment, in which biocides and oxygen do not effectively penetrate (1). The efficacy of biocide treatments is routinely assessed by quantitating the numbers of SRB using standard cultivation methods, or molecular probes. These enumeration methods may lead to erroneous conclusions since the presence of other sulfide-producing bacteria may be detected with these methods. Biocide effectiveness should be assessed by determining its effect on the activity in question, sulfide production.

New technology is needed to address some of the limitations inherent with the use of conventional methods to control microbial sulfide production. Our approach is to manipulate the ecology of the system to prevent the accumulation of sulfide by coupling its oxidation to the reduction of nitrate. The addition of nitrate has been shown to inhibit sulfide production in many environments (6). Thus, even if SRB or other sulfide producers are present, the accumulation of the unwanted product of their metabolism, sulfide, is prevented. This is done by the addition of nitrate and a sulfide-resistant strain of *Thiobacillus denitrificans*, strain F, that can oxidize sulfide to sulfate by reducing nitrate to nitrogen gas. Here, we present a short review of the applications of *T. denitrificans* strain F in the treatment of sour gas and water, and in the control of bionic sulfide production.

MICROBIAL CONTROL OF SOUR GAS

Thiobacillus denitrificans is an obligate autotroph and facultative anaerobe that uses reduced sulfur compounds as energy sources, and oxidizes them to sulfate. Under anaerobic conditions, nitrate is used as a terminal electron acceptor and is reduced to nitrogen (N_2) (equation 1):

$$5\ HS^- + 8\ NO_3^- + 3\ H^+ \text{ --> } 5\ SO_4^= + 4\ N_2 + 4\ H_2O \qquad (1).$$

T. denitrificans is readily cultivated in a mineral salts medium with CO_2 as the sole carbon source, either aerobically and anaerobically, in batch and continuous reactors, on gaseous H_2S, under sulfide-limiting conditions (7-10). The maximum loading rate for H_2S oxidation under anaerobic conditions was 5.4 to 7.6 mmoles H_2S $hr^{-1}g^{-1}$ of biomass. Under aerobic conditions, the maximum loading rate was much higher, 15.1 to 20.9 mmoles H_2S $hr^{-1}g^{-1}$ of biomass. No H_2S was detected in the outlet gas, even thought the residence time of a bubble of feed gas (average diameter of 0.25 cm) was 1 to 2 sec. A microbial process for the removal of H_2S from gases based on contact of the gas with a culture of *T. denitrificans* has been proposed (7).

SULFIDE TOLERANT STRAIN

Sulfide concentrations as low as 100 to 200 μM inhibit the growth of the wild-type strain of *T. denitrificans* (ATCC 23642) on thiosulfate (11). Complete inhibition was observed at initial sulfide concentrations of 1 mM. Clearly, any process for the treatment of sour gas or water would be more resistant to upset if a sulfide-tolerant strain of *T. denitrificans* were available.

Sulfide- and glutaraldehyde-resistant strains of *T. denitrificans* were isolated by selective enrichment from cultures of the wild-type (11). The sulfide tolerant strains were subjected to repeated exposure to increased levels of sulfide, and glutaraldehyde. At each step, only the tolerant strains survived and grew. Eventually, strains were obtained which grew at sulfide concentrations up to 2.5 mM. One strain, strain F, was chosen for further study. The growth rate and final absorbance of strain F in thiosulfate medium with up to 1 mM sulfide was similar to controls without sulfide. In medium with 1.5 mM sulfide, strain F grew after a 3 day lag. No growth of the wild-type strain of *T. denitrificans* was observed in medium with 1 mM sulfide. Strain F also grew in medium with glutaraldehyde concentrations of 25 to 40 ppm, concentrations that were lethal to the wild-type strains.

MICROBIAL TREATMENT OF SOUR WATER

Inorganic sulfides (H_2S, HS^-, $S^=$) often contaminate co-produced waters in oil fields. These sulfide-laden waters are usually treated by "air-stripping", which simply converts a water pollution problem to an air pollution problem. This type of pollution problem may one that can be treated directly by our new microbial technology.

The sulfide-tolerant strain of *T. denitrificans* immobilized with heterotrophic floc-forming bacteria successfully treated sour water containing 25 mM soluble sulfides. An aerobic up-flow bubble reactor run at retention times of 1.2 to 1.8 hours was used, and the sulfide-laden water was supplemented only with mineral nutrients. The molar sulfide feed rate was more important than the hydraulic retention time, or the influent sulfide concentration, in determining the sulfide oxidation capacity of the reactor. At a biomass concentration of 4 g liter $^{-1}$, the reactor operated without upset for a period of nine months at a molar sulfide feed rate of 12.7 to 15.4 mmole hr $^{-1}$.

CONTROL OF BIONIC SULFIDE PRODUCTION

T. denitrificans strain F was successfully grown in co-culture with the sulfate-reducing bacterium, *Desulfovibrio desulfuricans*, both in liquid culture and through Berea sandstone cores without the accumulation of sulfide (Tables 1) (12). Microbial sulfide production by an enrichment from an oil field brine was prevented by the presence of this sulfide-resistant strain F. Mass balances showed that strain F stoichiometrically oxidized the sulfide produced by *D. desulfuricans* and the oil field brine consortium to sulfate. The effectiveness of strain F was due to its ability to grow and use sulfide at levels that were inhibitory to the wild-type strain of *T. denitrificans*. There are many sulfide-oxidizing bacteria, but these bacteria are usually inhibited when H_2S concentrations reach a nuisance level. Strain F removed sulfide not only in cultures of *D. desulfuricans* with lactate as the energy source, but also in cultures with a mixture of sulfate-reducing bacteria which uses lactate and the products of lactate metabolism, acetate and H_2, for sulfide production.

Strain F of *T. denitrificans* grew through Berea sandstone cores (Table 1). Its penetration time was roughly 0.4 cm/day, which was much faster than that observed for *D. desulfuricans*, and the organisms present in the oil field enrichment. In co-culture, strain F and the sulfide-producing bacteria grew through the core together. This is important because it suggests that strain F uses sulfide as it is produced, preventing a buildup of sulfide. The slow growth of *D. desulfuricans* through sandstone may be a general property of SRB since an oil field consortium that contains several types of sulfate reducers also penetrated the cores slowly. If this is the case in the reservoir, then the production of sulfide may be a localized near the well-bore, and not deep within the reservoir, which

suggests that the use of strain F to control sulfide production may indeed be feasible since only the area near the well-bore needs to be treated.

Because *T. denitrificans* strain F is a chemoautotrophic bacterium, no additional organic nutrients are needed to support its growth. This will limit the growth of any indigenous organisms present which might require organic nutrients. Because it is a facultative anaerobe, *T. denitrificans* could be used not only in strictly anaerobic environments, but may be effective at utilizing H_2S which diffuses into the aerobic zone. Anaerobic corrosion by sulfate-reducing bacteria occurs at neutral pH, which is the optimal pH for the growth of strain F.

Limiting factors in the growth of *T. denitrificans* strain F, and its application to control sulfide production in oil and gas reservoirs include temperature, salinity, and the concentration of soluble organic compounds. *T. denitrificans* grows optimally at 30°C, but the rate of growth declines rapidly at higher or lower temperatures. Temperatures above 40°C completely inhibit growth, although cells remain viable at 45°C for 5 hr., suggesting that the use of strain F would be restricted to formations with temperatures below 45°C. Thirty-six percent of the reservoirs in Oklahoma have temperatures below 45°C, whereas 23% of the reservoirs in Texas, New Mexico, and Wyoming have temperatures below 45°C (13). *T. denitrificans* strain F does not grow in medium with salt concentrations above 3%, which would limit its use in many Oklahoma reservoirs, since the average salinity of Oklahoma reservoirs is 9%. States, such as California, Colorado, and Wyoming, have average salinities below 3%, and could be treatable with strain F. Even though strain F does not grow at thermophilic temperatures, or in highly saline media, there are still a large number of reservoirs in the U. S. that could be treated with strain F.

APPLICATIONS TO SULFIDE-PRODUCING BIOFILMS

The ability of strain F to establish itself, and to control sulfide production in porous rock biofilms was tested (14). One experimental system used consisted of cores and formation water from an underground gas storage facility. The core system contained three cylindrical cores of St. Peter sandstone connected in series. Formation water was injected into the core at a rate of 75 ml hr^{-1}, to give a hydraulic retention time of about 3.2 hr. Prior to the inoculation of the core system with strain F, formation water was supplemented with 40 mM nitrate. After inoculation with strain F, formation water with 10 mM nitrate and various inorganic nutrients, including potassium phosphate, magnesium sulfate, calcium chloride, ammonium chloride, and sodium bicarbonate, was used (14).

The results of this study are summarized in Table 2. Influent and effluent sulfide concentrations before the addition of nitrate to the formation water, and inoculation with strain F began were similar, indicating that little or no sulfide production occurred within the core. The injection of nutrients needed to support the growth of *T. denitrificans* did not simulate sulfide production, again

suggesting that little of no sulfide production occurred in the core system. The addition of nitrate alone reduced effluent sulfide concentrations by about 40%. Nitrate consumption was observed at this time, indicating that indigenous microorganisms were present that oxidized sulfide using nitrate as the electron acceptor.

The core system was inoculated with strain F several times, and various mixtures of formation water and *T. denitrificans* growth medium were injected into the core. Formation water supplemented with inorganic nutrients and nitrate was then injected into the core system. Effluent sulfide concentrations were much lower than that observed when only nitrate was added (Table 2), indicating that strain F was more effective than the indigenous organisms in using sulfide. There was a substantial decrease in the effluent concentration of nitrate, and a substantial increase in effluent sulfate concentrations, consistent with the oxidation of sulfide to sulfate coupled to the reduction of nitrate by strain F. The amount of sulfate detected in the effluent was much higher than that expected based on the amount of sulfide used, and on the influent sulfate concentration. This suggested that sulfur compounds that accumulated within the core system were metabolized by strain F. Strain F can use iron sulfide precipitates (11). High effluent concentrations of strain F ($>10^7$ cells ml^{-1}) were observed 7 days after the injection of formation water with nitrate and inorganic nutrients was resumed. Thus, strain F was maintained, and metabolically active within the rock biofilm.

The next step was to demonstrate whether strain F would be effective in a SRB biofilm that was actively producing sulfide. An experimental system similar to that described above was used, except that two core systems operated at nearly identical flow rates were used, and each core system had two instead of three St. Peter sandstone cores. Two different nutrient supplementations to the formation water were used to stimulate sulfide production, formation water with 10 mM acetate, and formation water with 5 mM lactate, and inorganic nutrients (KH_2PO_4, $MgSO_4 \cdot 7\ H_2O$, NH_4Cl, $CaCl_2 \cdot 2\ H_2O$, $NaHCO_3$, and NaCl), at concentrations found in *T. denitrificans* growth medium (7). For both cases, 10 mM sodium nitrate was added, and a flow rate of 0.1 ml hr-1 was used.

Each core system was inoculated with a mixed population of SRB enriched from the formation water using a lactate-sulfate mineral salts medium. After the SRB population was established in the core systems, formation water with 10 mM acetate and 5 mM nitrate was injected into each core system for one week. No consumption of nitrate was observed, and effluent sulfide concentrations of each core system remained similar those observed prior to nitrate addition. No strain F-like organisms were detected. These results indicated that microorganisms capable of using nitrate were not present in the two core systems.

The test core system was inoculated with *Thiobacillus denitrificans* strain F, and the test core system received formation water with 10 mM acetate and 5 mM nitrate for five weeks. The control core system received formation water with 10 mM acetate for 3 weeks, and then received formation water with 10 mM acetate and 5 mM nitrate for two weeks. Data shown in Table 3 were taken during the fifth week of injection of formation water with 10 mM acetate. The effluent sulfide concentration of the test core system was 67 μM five weeks after inoculation with strain F (Table 3). Effluent sulfide concentrations in the control core system were

higher, about 240 μM. Nitrate consumption was observed in the test core system, but not in the control core system. Numbers of SRB in the effluent of the control and test core systems were similar, about 10^7 and 10^8 cells/ml, respectively. The numbers of strain F-like organisms in the effluent of the test core system increased from 10^3 cells per ml immediately after inoculation to 10^4 cells per ml 2 weeks after inoculation. No strain F-like organisms were detected in the effluent of the control core system.

When formation water supplemented with lactate and inorganic nutrients was used, sulfide production in the control core was greatly stimulated. During the first three weeks, effluent sulfide concentrations, ranging from 3060 to 3780 μM, were observed. During this time, sulfide production in the test core system remained low, <270 μM. After five weeks, sulfide production in the control core system was about 1000 μM (Table 3). However, sulfide production in the test core system was <170 μM. About 5 times less sulfide was made in the test core system inoculated with strain F compared to the control core system. Growth was observed in some of the thiosulfate/nitrate mineral medium dilution bottles inoculated with effluent from the control core system during this period. Microscopic examination showed that the predominant morphology in these bottles was similar in morphology to several SRB (2). The numbers of strain F-like organisms in effluents of the test core system were always 3 orders of magnitude greater than the numbers of nitrate users detected in effluents from the control core system.

Increasing the nitrate concentration in the formation water from 10 to 20 mM did not markedly affect the sulfide production in either of the two core systems. The control core system produced about 1000 μM sulfide, while the test core system produced 100 to 200 μM sulfide. However, little or no nitrate was consumed in the control core system at this higher nitrate concentration, and the numbers of nitrate-using bacteria detected in the effluent of the control core system decreased to about 10 cells per ml. In the test core system, levels of strain F-like organisms remained high, 10^5 to 10^6 cells per ml, and about the same amount of nitrate was consumed (5 mM) as was observed when 10 mM nitrate was used. Thus, strain F was maintained for a longer period of time than were the indigenous nitrate-using organisms in the control core system.

CONCLUSIONS

The *Thiobacillus denitrificans* strain F was more effective than the addition of nitrate alone in controlling sulfide production by a porous rock SRB biofilm. Little or no plugging occurred during the course of this experiment, even after extended incubations (about eight months). The fact that nitrate consumption and high numbers of strain F were detected in the effluent of the test core system several months after inoculation showed that strain F remained metabolically active during extended periods of operation. These studies showed that a new technology based on the use of strain F to control sulfide production during the exploitation of oil and natural gas is effective and technically simple in its application.

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Table 1.
Growth and penetration of *D. desulfuricans* and *T. denitrificans* alone or in combination through Berea sandstone cores.

Culturea	Penetration time (days)	Sulfide		Blackening of core
		Distal Flask (μM)	Core[b] (μM)	
DD alone	25	300	200	yes
DD+F	25	0	0	no
F alone	17	0	0	no

[a] Abbreviations: DD, *D. desulfuricans*; F, *T. denitrificans* strain F.

[b] Berea sandstone cores had a diameter of 1.9 cm, lengths of 6.0 to 7.5 cm, permeabilities greater than 500 millidarcy, and pore volumes of 2.1 to 3.0 ml.

Table 2.
The effect of nitrate and inoculation with *T. denitrificans* strain F on the effluent sulfide concentration from core system with a hydraulic retention time of 3.2 hr.

Additions to formation water	Sample location	Sulfide (μM)	Nitrate (mM)	SRB (cells/ml)	Strain F (cells/ml)
None	influent	170	0.5	10^5	<10
	effluent	160	0.5	10^5	<10
Nitrate	influent	190	39.5	10^7	<10
	effluent	110	21.9	10^5	<10
Nitrate + Strain F + nutrients[a]	influent	160	10.6	10^7	10^7
	effluent	25	3.5	10^7	10^7

[a] Formation water was supplemented with inorganic nutrients, and inoculated with *T. denitrificans* strain F.

Table 3.
Efficacy of *T. denitrificans* strain F in controlling sulfide production by a porous rock biofilm.

Treatment[a]	Core system[b]	Sulfide produced (μM)	SRB (cells/ml)	Strain F (cells/ml)
Acetate + Nitrate	Control	244	10^7	10
	Test	67	10^8	10^4
Lactate + Nutrients + Nitrate	Control	1000	10^8	10^5
	Test	157	10^8	10^8

[a] Formation water was supplemented with 10 mM each of acetate and nitrate, or 5 mM lactate, 10 mM nitrate, and inorganic nutrients. Data were taken 5 weeks after the start of each treatment.

[b] Test core system was inoculated with *T. denitrificans* strain F; control core system was not inoculated with strain F.

Microbial Treatment of Refinery Spent Sulfidic Caustics

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ABSTRACT

Caustics are used in petroleum refining to remove hydrogen sulfide from various hydrocarbon streams. The resulting waste stream, called a spent-sulfidic caustic, has a pH greater than 12 and may contain 2-3 wt% sulfides in addition to various amounts of phenolic, amines and other organics. Spent sulfidic caustics from two Conoco refineries have been successfully biotreated at the bench and pilot scales resulting in neutralization and removal of active sulfides. Sulfides were completely oxidized to sulfate by the chemoautotroph *Thiobacillus denitrificans*. Microbial oxidation of sulfide produced acid which at least partially neutralized the caustic.

INTRODUCTION

Sodium hydroxide (NaOH) solutions are used in petroleum refining to remove hydrogen sulfide (H_2S) from various hydrocarbon streams. Once H_2S reacts with the majority of NaOH in the solution, the solution becomes known as spent-sulfidic caustic. Spent caustics typically have a pH greater than 12, sulfide concentrations exceeding 2-3 wt%, and a large amount of residual alkalinity. Depending on the source, spent caustic may also contain phenols, mercaptans, amines, and other organic compounds which are soluble or emulsified in the caustic (1). For example, a 20 wt% sodium hydroxide solution can be used to remove residual amounts of H_2S from natural gas after the majority of H_2S has been removed by the refinery gas plant amine unit (2). In this application, percent levels of amines can be found in the spent caustics due to amine carryover.

Currently, most spent-sulfidic caustics generated by refineries are either sent off-site to commercial operations for recovery or reuse (pulp and paper mills, for example) or for disposal by deep-well injection. Biological treatment in the refinery wastewater treatment unit is an inexpensive disposal option. However, many refineries do not have the wastewater treatment capacity to treat the entire amount of spent caustic generated and concerns regarding odors and toxicity frequently prohibit this practice.

Future regulatory changes could result in more stringent controls and increased cost for off-site management of spent caustic. In such an event, low cost on-site treatment options would be desired. Even without regulatory changes, current off-site transportation and disposal cost warrant further investigation of on-site management alternatives. Wet-air oxidation (WAO) is a commercially available process for on-site management of spent caustic; however, WAO can result in significant capital investment and high operating cost (3). WAO can be particularly expensive for spent-caustic streams from small to medium size refineries due to an insufficient economy of scale.

The objective of this work was to evaluate the feasibility of biologically treating refinery spent sulfidic caustic using a bioreactor containing a microbial culture augmented with the sulfide-oxidizing bacterium, *Thiobacillus denitrificans*. It is envisioned that this process could be implemented either by augmenting an existing refinery activated sludge unit so that it could handle higher concentrations of sulfides without toxicity or odor problems or by using a relatively small bioreactor which would be specialized for treating spent sulfidic caustic streams.

We have previously demonstrated that *T. denitrificans* can be readily cultured aerobically or anoxically at pH 7.0 and 30 C on H_2S (g) as an energy source at the bench scale in stirred-tank reactors (4-7). Complete oxidation of H_2S to sulfate was observed. *T. denitrificans* has also been flocculated by co-culture with floc-forming heterotrophs from an activated sludge system and used

to treat sour gas and sour water in stirred-tank reactors and bubble columns with biomass recycle (8-10). A sulfide-tolerant strain of *T. denitrificans* (strain F) has now been flocculated and used to biotreat refinery spent-sulfidic caustic from two Conoco refineries at the bench scale. Spent caustic from one of these refineries has also been successfully biotreated at the pilot scale (1000 gal or 3875 L).

MATERIALS AND METHODS

Organism and Stock Cultures

Thiobacillus denitrificans (ATCC 23642) was originally obtained from the American Type Culture Collection (Rockville, MD). A sulfide-tolerant strain (strain F) was isolated by enrichment as described previously (11). Stock cultures were grown anoxically in 10-mL culture tubes at 30 C in thiosulfate medium described previously (4). In this medium thiosulfate is the energy source, nitrate the terminal electron acceptor, biocarbonate the carbon source and ammonium ion the source of reduced nitrogen. The medium also contains a phosphate buffer and sources of Mg^{+2}, Ca^{+2}, Fe^{+3}, Mn^{+2} and trace elements.

T. denitrificans was flocculated by aerobic co-culture with floc-forming heterotrophs from a refinery activated sludge system as previously described (8).

Bench-scale Biotreatment of Spent Sulfidic Caustic

Five samples of spent sulfidic caustic were successfully biotreated in a 1.5-L stirred-tank reactor. Sample characteristics are given in Table 1. All samples were odorous and likely contained organic compounds that were not identified.

The bioreactor used for bench-scale biotreatment of spent caustics consisted of a B. Braun Biostat M fermenter. The reactor was initially charged with 1.5 L of the thiosulfate medium described above, without thiosulfate or nitrate, containing 1700 mg/L of flocculated *T. denitrificans*. The agitation rate was 180 rpm of the pH and temperatures were maintained at 7.0 and 30 C, respectively. The acid used for pH control was 10 N HNO_3. This particular acid was used so that acid addition could be monitored by following the nitrate concentration in the culture medium. The culture received a gas feed of 0.3-0.4 L/min of air with 5% CO_2. No nitrate is utilized under aerobic conditions (data not shown). The outlet gas was passed to a 500-mL Erlenmeyer flask where the gas was sparged into 300 mL of 0.3 wt% zinc acetate to trap fugitive H_2S from the bioreactor. A tee connection was located between the bioreactor of zinc acetate trap for gas sampling.

The feed reservoir consisted of a 250-mL graduated cylinder with a cork

stopper. Spent sulfidic caustic samples were diluted 1/5 with deionized water but not neutralized (pH > 12). Diluted caustic was withdrawn through a 0.32-cm stainless-steel tube that extended to the bottom of the cylinder. Feed was pumped to the bioreactor with a B.Braun FE 211 pump. The feed was introduced into the bioreactor at a point about 2.5 cm from the bottom of the vessel and adjacent to one of the agitator impellers.

At start-up, 150 mL of the process culture was removed from the bioreactor with the biomass recovered by centrifugation at 5000 g and 25 C and returned to the culture. The supernatant from this centrifugation was the initial sample for sulfate, ammonium ion, nitrate and COD determination. A sample for mixed liquor suspended solids (MLSS) determination was taken directly from the bioreactor after the biomass from the initial sample had been returned. At this time the feed pump was activated and a 1/5 dilution of spent sulfidic caustic (sample D1) was delivered to the bioreactor at approximately 7.2 mL/hr. The feed reservoir contained 150 mL of diluted caustic; therefore, the feed reservoir was emptied in 21 hrs. The reactor received no feed for the next 3 hrs. (The effective hydraulic residence time was 10 days.) At the end of this time, and each day thereafter, the feeding procedure was repeated with 150 mL removed from the bioreactor, the biomass recovered and returned to the culture. At the end of the 7th day of operation (after a total of 1050 mL of diluted caustic had been fed to the reactor) the agitation and gas feed were turned off and the biomass allowed to settle under gravity. The biomass settled to 25% of the original volume in less than 10 min. The clarified liquor was then siphoned off and replaced with fresh medium (described above) to a final volume of 1.5 L. The agitation and aeration were then resumed. At this time 150 mL of the culture were removed, the biomass recovered and returned to the culture and the feeding schedule resumed as described above using a second sample of caustic (D2). This replenishment of the culture medium was also repeated after 5 days of operation at which time the caustic feed was changed to the D3 sample of the duration of the experiment. The experiment was terminated after 21 full days of operation, on the D series feeds.

The PC1 and PC2 samples were biotreated at the bench scale at a later time using a second flocculated culture of *T. denitrificans* strain F developed for this purpose. The bioreactor was operated as described above for 6 days using PC1 as feed and 10 days using PC2 as feed.

Pilot-scale Biotreatment of Spent Sulfidic Caustic

Pilot-scale biotreatment of spent sulfidic caustic was conducted in a 3.8-m^3 stainless steel, milk-holding tank manufactured by the Paul Mueller Co. (Springfield, MO). The tank was horizontal and semi-cylindrical, 170 cm deep and 660 cm long on the inside. The tank was jacketed with cooling/heating coils running length-wise in the jacket annular space. A 2-hp (horse power) variable speed DC motor and gearbox were mounted on a platform which bridged the center of the vessel. The motor drove a paddle-type stirrer which was 81 cm in

diameter and 12 cm wide. The agitation rate was 50 rpm. On either side of the stirrer platform were stainless steel lids which completely closed the top of the vessel. The tank was modified by fitting with stainless-steel baffles, each 1/10 of the major or minor dimensions of the tank, and a sparger. The sparger was fabricated from 2.5-cm stainless-steel tubing in a U-shape. It was fed with air at the bottom of the U through a 2.5-cm stainless-steel tube which extended through the wall of the vessel at the center and bottom. The sparger was centered under the stirrer with the branches of the U equal in length to the stirrer diameter. The U branches had equally spaced 0.32-cm holes drilled on the bottom such that the total hole area on each branch was two times the cross-sectional area of the tube.

Air was fed to the reactor using both a Fugi model VFC504A-7W ring compressor and line air from an in-house compressor. About 0.85 standard m^3/min of air was supplied by the blower to the sparging system. Air from the blower was cooled with a Speedaire Model 5Z267 after-cooler or heat-exchanger using house water at 15 C. Line air was introduced into the reactor at each end with two supplemental spargers which consisted of 1.25-cm stainless-steel tubes bent at one end to produce a 0.3-m section which was perforated with 0.32-cm holes. An additional 0.42-0.57 standard m^3/min could be provided to the reactor in this manner.

Temperature control in the 3.8-m^3 tank was achieved by circulating water from a Neslab Model HX-300 refrigerated recirculator through the jacket coils. Some heating could also be obtained as needed by reducing the cooling water flow rate to the blower after-cooler, thereby increasing the temperature of the air. The temperature was maintained at 30 $\pm$ 1 C. The pH was monitored and controlled at 7.0 $\pm$ 0.05 by a Cole-Parmer (Chicago, IL) Model 5651-50 pH meter/controller which activated a Cole-Parmer Chem-Feed Pump to deliver acid or alkali as needed.

The 3.8-m^3 stirred-tank reactor was utilized for pilot-scale biotreatment of spent sulfidic caustic as follows. About 40 L of the concentrated suspension of flocculated *T. denitrificans* strain F, produced as previously described (12), was used to inoculate 3.0 m^3 of thiosulfate-free medium. The initial MLSS was 630 mg/L. Spent sulfidic caustic (samples PC2 and PC3, about 180 L of each) was fed (undiluted) from 0.23-m^3 barrels by a Cole-Parmer Chem-Feed Pump (Model 5000-076) connected to a Chron Trol Model CD-4 timer (Lindberg Enterprises, San Diego, CA). Since the desired feed rate of 30 mL/min was less than the lowest steady flow rate of the pump, the timer was used. At a pump feed rate of 150 mL/min, the timer switched on the pump for 12 sec every minute giving an effective feed rate of 30 mL/min. The caustic was conveyed to the reactor through 0.95-cm PTFE tubing and introduced below the liquid surface near the impeller tip. The temperature was maintained at 30 C and pH at 7.2 $\pm$ 0.1 with 85% H_3PO_4, industrial grade (Delta Distributors, Dallas, TX). The agitation rate was 50 rpm and aeration rate was about 1.1 standard m^3/min (blower + line air). The culture was operated with spent sulfidic caustic feed intermittently during the evenings and on weekends because of the odor from the caustic. When not

receiving a caustic feed (10-12 hrs at a time) the culture was maintained at temperature with aeration. The total operating time with spent caustic feed was 200 hrs.

Analytical

The hydrogen sulfide concentrations in the outlet gas of cultures in the B. Braun Biostat M and the vapor space of the 3.8-m^3 stirred-tank reactor were estimated using Gastec Analyzer tubes (Yokohoma, Japan). The range of the analyser tubes was 2.5-60 ppm $\pm$ 2 ppm using 100-mL samples.

Total aqueous sulfide (H_2S, HS^- and S^{-2}) was determined colormetrically using the methylene blue method (10). The medium in the 3.8-m^3 reactor was sampled for sulfide using sulfide ion analyzer tubes (Yokohoma, Japan) with a range of 1-100 mg/L. Sulfate, elemental sulfur, ammonium ion, nitrate and COD were determined as previously described (4). The MLSS concentration was determined by filtering known volumes (5 mL or 10 mL) of the culture medium through tared, prewashed Whatman GF/C glass fiber filters (13).

Methyl diethanolamine (MDEA) in culture medium samples was determined by gas chromatography. A glass column packed with 60/80 Carbopack B/4% Carbowax 20 M/0.8% KOH manufactured by Supelco (Bellafonte, PA) was used for the analysis. The operating conditions were: oven temperature, 240 C; injector temperature, 250 C; detector (FID) temperature, 250 C; carrier gas, He at 38 mL/min; and sample size, 1μL. The retention time for the MDEA was about 5.4 min. Standards were prepared gravimetrically using MDEA from Aldrich Chemical Co. (Milwaukee, WI).

RESULTS AND DISCUSSION

Bench-scale Biotreatment of Spent Sulfidic Caustic

It is important to note that the spent sulfidic caustic was introduced into the bioreactor without neutralization. Sulfide oxidation by *T. denitrificans* is acid producing (4). Therefore, if the reactor is operated on a sulfide-limiting basis at least partial neutralization of the added caustic can be achieved by the oxidation reaction if the reaction is sufficiently fast. This was indeed the case in this experiment. During the entire course of the experiment the pH was maintained at 7.0-7.1 with only a small amount of acid addition as shown in Table 2. All of the acid produced by sulfide oxidation by the organism was neutralized by the hydroxide ion in the samples. The amount of HNO_3 required to maintain the pH in the 7.0-7.1 range was dependent on the extent to which the alkalinity in the sample exceeded the acid produced by sulfide oxidation. Greater addition of nitric acid was required when the D1 sample was used as feed because of the much

greater alkalinity of the sample (Table 1).

Sulfate was observed to accumulate in the culture medium as each sulfidic caustic was fed to the bioreactor. A sulfur balance showed complete conversion of sulfide to sulfate (Table 2). No elemental sulfur was detected in the culture medium and no H_2S was detected in the outlet gas or collected in the zinc acetate trap.

Ammonium ion was consumed as a source of reduced nitrogen as *T. denitrificans* strain F grew at the expense of oxidation of sulfides in the caustic as an energy source when the D1 and D2 samples were used as feeds. However, there was an increase in the ammonium ion concentration when the D3 caustic sample was used as feed. The COD concentration in the reactor increased as sulfidic caustic was fed to the bioreactor when the D1 and D2 samples served as feed. However, when the D3 sample was used as feed, the COD initially started to rise but then sharply declined. The MLSS concentration increased as expected during growth on the D1 and D2 samples indicating that *T. denitrificans* used sulfides in the caustic as an energy source to support growth. Biomass yields (Table 2) were comparable during this time to yields observed with H_2S (g) as an energy source (7). However, when the D3 sample was used as feed the MLSS concentration rose more sharply and biomass yields per mole of sulfide oxidized were much higher (Table 2).

During growth on the D1 and D2 samples the MDEA concentration increased with each feeding indicating that MDEA was accumulating without degradation. However, when the D3 sample served as feed MDEA was detected in the medium for two days at low levels and then not detected again for the duration of the experiment. This suggests that the culture became acclimated to the MDEA and had begun to degrade the amine.

The unusual ammonium ion, COD and MLSS results obtained when the D3 sample was used as feed are now understandable in light of the MDEA results. The surge in ammonium ion concentration was due to the liberation of ammonia during degradation of MDEA. The low COD resulted from the corresponding lack of MDEA accumulating in the culture medium. The higher rates of MLSS accumulation compared to the rate of sulfide feed resulted from the rapid growth of heterotrophs on MDEA once they had become acclimated.

Results obtain from biotreatment of sample PC1 and PC2 were very similar to those obtained with samples D1 and D2. Because of the shorter duration of these experiments, the culture did not acclimate to MDEA thus MDEA accumulated (up to 2000 mg/L) in the culture medium throughout while PC1 served as feed. However, the presence of MDEA did not interfere with sulfide oxidation (Table 2). PC2 did not contain MDEA. As seen in Table 3 much more HNO_3 per mole of sulfide oxidized was utilized in biotreating samples PC1 and PC2 compared to D1, D2 and D3. This is due to the lower sulfide concentrations and higher hydroxide in concentrations in these samples (Table 1).

Note, however, that the moles of acid produced per mole of sulfide oxidized was roughly the same for all samples (Table 2).

Pilot-scale Biotreatment of Spent Sulfide Caustic

Sulfate accumulated in the reactor medium as caustic was fed to the pilot-scale reactor. No hydrogen sulfide emissions were detected from the reactor at any time during 200 hrs of operation and no sulfide was detected in the culture medium. The overall sulfate/sulfide ratio observed was 1.3. However, only the soluble sulfide concentrations in these samples were used to calculate this ratio. These samples contained copious amounts of iron sulfides. Iron sulfides in the feed were most notable when feed was initiated from a new barrel (after some agitation in getting the barrel in place) and after about 75% of the caustic in each barrel had been pumped out. In the latter case the solids had concentrated at the bottom of the barrel. In fact, the sludges were so viscous at the bottom of the barrel that they could not be pumped out.

The elemental sulfur concentration in the reactor medium averaged about 0.3 mg/L except for one five hour period when we attempted to double the caustic feed rate. This increase in feed rate caused an upset condition in which the elemental sulfur concentration became high enough to give the culture a white color. The caustic feed was stopped and the culture aerated overnight. The next day the elemental sulfur was gone (oxidized to sulfate) and the caustic feed was resumed at 30 mL/min with no further difficulties.

The MLSS concentration rose rather sharply following initiation of caustic feed; however, the rate of increase slowed after about 70 hrs. This may have been due to increased solids in the feed during this time since the barrel was agitated somewhat during setup. Once the iron sulfide solids settled down below the intake to the pump the solids concentration in the feed fell. The overall biomass yield was 10.8 g/mole of soluble sulfide. The ammonium ion concentration was seen to decrease as caustic was fed to the reactor as ammonium ion was used as a source of reduced nitrogen by the organisms (data not shown). The COD concentration was seen to increase as caustic was fed to the reactor. This is likely due to the presence of an unidentified organic compound present in the caustic which was not degraded by the culture. Such a compound was detected (but not identified) by gas chromatography. About 2.8 moles of H_3PO_4 were required per mole of soluble sulfide in the caustic to maintain the pH at 7.2. A total of 360 L of refinery spent sulfidic caustic was successfully treated in about 200 hours of run time.

CONCLUSIONS

Refinery spent sulfidic caustics have been successfully biotreated at the bench and pilot scales resulting in neutralization and removal of reactive sulfides. Spent caustic could be fed to the bioreactor undiluted and without prior neutralization. Future work will incorporate mercaptan contaminated caustics.

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Table 1
Characteristics of Spent Sulfidic Caustic Samples*

Sample	Sulfide (M)	COD (mg/L)	MDEA (wt%)	OH^-(M)
D1	1.06	82100	2.37	2.60
D2	1.05	113800	3.17	1.04
D3	1.06	107000	3.81	1.03
PC1	0.60	73300	2.08	2.46
PC2	0.58	40200	-	2.91
PC3	0.73	46300	-	2.80

(MDEA = methyl diethanolamine)

* D1, D2 and D3 were obtained from the Conoco Denver Refinery; PC1, PC2 and PC3 were obtained from the Conoco Ponca City Refinery.

Table 2
Stoichiometry of Sulfide Oxidation by *T. denitrificans* in a Bench-scale Fed-batch Reactor with a Feed of Spent Sulfidic Caustic

Sample	SO_4^{-2}/S^{-2} (mole/mole)	HNO_3/S^{-2} (mole/mole)	H^+ prod/S^{-2} (mole/mole)	g MLSS/mole S^{-2}
D1	1.00	1.06	1.39	4.1
D2	1.07	0.048	0,94	6.1
D3a	1.10	0.040	0.94	18.3
D3b	1.01	0.040	0.94	15.9
PC1	0.98	3.0	1.10	8.5
PC2	1.00	4.0	1.02	11.8

HNO_3/S^{-2} is the moles HNO_3 per mole sulfide oxidized required to maintain the pH at 7.0-7.1.
H^+ prod/S^{-2} is the moles of acid produced per mole of sulfide oxidized.

Perspectives on NORM Wastes

NORM Contamination in the Petroleum Industry

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NORM contamination is one of the emerging environmental issues of the 1990s. The perceived need to protect the health and safety of employees, the public and the environment, and the need to control the spread of contaminated materials into commerce and unrestricted areas, have led regulatory agencies to develop regulations for the control of NORM. Major petroleum producing states, e.g., Louisiana, Mississippi, Texas and Arkansas have enacted regulations and several other states will have regulations in 1994. Federal regulations are probable in the future as the Environmental Protection Agency begins the regulatory process with NORM contaminated site cleanup regulations with the probability of more NORM regulations to follow. Disposal of NORM wastes continues to be a major problem with large volumes of NORM-contaminated wastes being stored awaiting cost-effective disposal options. Recent history, validated by abundant case law, evidences that the reality of an emerging environmental hazard invariably breeds personal injury and property damage litigation. Petroleum companies, both large and small, must be aware of the possibility of NORM contamination in their operations and prepare a program for its control. Compliance with the regulations will be essential to help minimize the effects of future litigation.

Introduction

NORM has been described as one of the emerging environmental issues of the 1990s. The perceived need to protect the industry worker and the public from radiation and radioactivity and to control the spread of contaminated materials into commerce and unrestricted areas have led regulatory agencies to develop regulations for the control of NORM.

Naturally occurring radioactive material (NORM) contamination has long been an environmental burden in nearly all petroleum facilities. Radon and radon decay products, more prevalent in natural gas production and processing, were identified as contaminants by the oil industry in 1971. Radium, the most common radioactive scale pollutant in oil production operations, was recognized as such in Russia in the 1960s, in the North Sea in 1981, and in the United States in the middle 1980s.

The fact that naturally occurring radioactive materials exist at many oil and gas producing facilities throughout the world has been a matter of scientific record since the early 1930s when elevated levels were measured in Russian oil fields. This natural radioactivity has been exploited for monitoring well performance for more than 40 years (Campbell 1951, Gott and Hill 1953 and Fertl 1983).

History of NORM Contamination in the Petroleum Industry

The coprecipitation of radium with barium sulfate was studied and reported in the Journal of the American Chemical Society as long ago as 1925 (Doerner and Hoskins 1925). Campbell reported on the occurrence of increased natural radioactivity over time due to the buildup of a "radioactive crust" in producing wells in 1951. In 1932 and 1954 it was reported that radium bearing precipitates in oil field fluids resulted from the coprecipitation of radium with barium and strontium because of changes in solubility during the process of pumping oil field brines (Vernadskii and Khlopin 1932 and Gott and Hill 1954). These precipitates were also reported to have resulted from the mixing of two waters, one rich in strontium and barium and the other in sulfate. There have been reports since the early 1950s of anomalous radioactive "hot spots" in production wells, particularly in older wells where the volume of water being produced had markedly increased as compared with earlier production. Difficulties in calibrating gamma ray logging tools were also

indications of NORM-contaminated scale in the production piping.

In 1951, Campbell described the formation of radioactive crusts (scale) as:

In many cases, after the well has produced for many years from a particular zone and in time has produced tremendous quantities of water, necessitating work-over, a gamma ray survey will show an extremely high radioactive intensity opposite the sand of interest, which is caused by a radioactive crust in the perforated zone. The development of such crusts is usually associated with a reduction in reservoir pressure and the production of water. Formation waters and oil, supersaturated with salts of radioactive materials release the salts, which are deposited to form the crusts. This radioactive crust may be both on the inside of the casing, as well as in the casing perforations. The crust is built up as a deposit of radioactive minerals as a result of the salt water reacting chemically with iron oxides of the casing.

In 1980, Maher interpreted high gamma ray readings from radioactivity logs as indicating scale formation containing a natural radioactive substance that could be radium associated with barium sulfate scale as suggested by Gates and Caraway in 1965. Fertl (1983) stated in an article that *precipitation of radioactive salts in cased wells is well known. Such radioactive salts are usually found to coprecipitate with barium sulfate, since barium is a chemical analog to radium and has a very low solubility.* Fertl included field examples from South and North America in his article.

Radioactivity in oil well scales was reported in more than 60 fields in southeastern Kansas in 1965 (Gates and Caraway 1965). The scales analyzed were primarily barium sulfate, probably formed from barium in the formation water combining with sulfate from injected sea water. Radioactive scale or crust was observed in a central Mississippi well in 1972, in an east-central Mississippi well in 1973 and in an oil well in southeastern Louisiana around 1970 (Doering and Smith 1974).

In the former Soviet Union, radioactive scale contamination has been found in oil fields of Western Siberia, the Northern Caucasus, Apsheron, and other regions (Broder 1993). In the Tararstan oil field in the mid 1960s, 22% of tested wells were contaminated with NORM scale. For unknown reasons, the number of wells containing contaminated scale sharply decreased during the 1970s and only isolated cases of contaminated scale occurred in these wells until 1990. The number of wells containing NORM scale is presently increasing again in the Tararstan oil field (Diyashev 1994).

In 1981, radiation alarms on a production platform in the North Sea sounded while pipe was being pulled. Personnel on the platform assumed the alarms were triggered by a breached logging source. NORM contamination of the scale, however, was the source of the radiation. Although radioactive contamination of scale had been observed previously, it was this North Sea event that led to regulations for NORM control in the United Kingdom and later in the United States.

In the United States, although radioactive scale had been noted earlier in Kansas, Mississippi and Louisiana, the presence of NORM in mineral scale deposits came to the attention of industry and government in the spring of 1986 when during a routine workover of a well in Mississippi, barium sulfate deposited in production tubing was found to contain radium and thorium. Subsequently, used production pipe used for bleachers and playground equipment in Mississippi and Louisiana was found to be contaminated with NORM. Subsequently, a scale-contaminated site where some samples contained as much as 7000 pCi/gram of radioactivity was found in a Mississippi field. Soon similar findings in their state led Louisiana to develop regulations to control what they perceived to be a serious environmental problem.

The Source of NORM in the Petroleum Industry -- Radium NORM

The source of most oil and gas radium contaminated scale and sludge NORM is dissolved radium that is transported to the well in the produced water. Dissolved radium either remains in solution in the produced water, or under proper conditions coprecipitates with barium, strontium, or calcium to form either hard sulfate scales in the well or more granular silicate and carbonate sludges often found in surface equipment in contact with the produced water.

The uranium and thorium parent radionuclides within the formation are relatively insoluble whereas the radium decay products of uranium and thorium may be considerably more soluble, depending on the specific anions, particularly chlorides, within the formation. This enhanced solubility may result in increased mobility by allowing the soluble radium materials to be transported through the geological formation in the water and be produced at the well with the other petroleum fluids and may contaminate scale in the tubing or scale and sludges in surface equipment in contact with the produced water. In contrast, only trace amounts of uranium-238, thorium-232, lead-210, polonium-210, and other NORM radionuclides are typically transported to the surface in the produced water.

High radium concentrations in water produced with oil and gas received much attention in Russia during the 1930s but did not attract much attention in the United States until the work of Gott and Hill (1953). It had been known for some time in the United States that gamma ray logs showing abnormally high radioactivity were associated with oil and gas deposits. These were used for geological interpretations and correlations but were not associated with water until anomalies between gamma ray logs in new wells when water production was usually small were compared to logs of wells that had been producing for some time and water production had increased significantly (Campbell, 1951).

The earlier work in the 1930s in Russia gave impetus and added interpretation to more modern work with increasingly sophisticated equipment. Nikitin and Komleff (1930) investigated the radioactivity of produced water in oil fields of Baku and Daghestan. In the region of Ferghana, Russia, Nikitin (1932) found that the concentration of radium in oil field waters varied with productivity, depth, and the time that wells had been produced. Vernadskii (1932) reported that radium was highest in the most productive wells and was lowest in exhausted oil sections. Several other measurements of radium in produced water were done by Russians in the 1930s and continued through the 1960s.

There is limited literature on the naturally-occurring radionuclides in produced water of the United States The important papers reporting on radioactivity in produced water include Gott and Hill (1953), who measured the radium content in over 300 oil, natural gas and helium wells in southeastern Kansas. Armbrust and Kuroda (1956) presented data on the radioactivity in brines and gas associated with oil and gas in Oklahoma. The radium concentrations were as high as 1620 pCi/liter for radium-226. The Pierce, Gott, and Mytton (1955) report is a very comprehensive and lengthy study of the Panhandle gas field in Texas. The radium-226 content of brines from 75 wells ranged up to 1560 pCi/liter. The status of the radionuclide content of produced water up to 1989 is summarized in "Radionuclides in Produced Water - A Literature Review" by Earl Snavely, Jr. August, 1989 and available from the American Petroleum Institute. Snavely reported the radium concentrations in produced water vary from undetectable levels to 2,800 pCi/liter. A recent study of oil-field produced water discharged to the Gulf of Mexico offshore Louisiana found average total radium concentrations of 589 pCi/liter (Brookhaven National Laboratory 1992). Although only a limited number of samples were collected, brine produced at oil and gas facilities in Michigan measured as high as 29,000 pCi/liter (Minaar 1992).

Although the initial production of oil and gas from a reservoir is typically dry, as the natural pressure within the petroleum bearing formation falls, formation water within the reservoir may be produced with

the oil and gas. NORM contamination is a non-linear event. As an oil field ages, the production of water usually increases. Since radium is a "constituent" of the water, as the production of water increases, the formation of NORM usually increases as well.

Radon / Radon Decay Product NORM Contamination in the Petroleum Industry

Natural gas was reported to be radioactive as early as 1904 (Satterly and McLennan, 1918). The source of the radioactivity was identified as radon. A detailed survey was made of radon concentrations in natural gas wells in the West Panhandle Field, Texas, and in the gases from 66 other natural gas fields in central and southwestern United States (Faul et al, 1954). Subsequently, radon has been found to be a contaminant in nearly all natural gas reservoirs worldwide. However, it wasn't until 1971 that the petrochemical and petroleum industries acknowledged that radon and the radon radioactive decay products were seriously contaminating the natural gas industry, especially the natural gas liquids plants. Although radon had been recognized much earlier as a contaminant of natural gas, it wasn't until 1971 that it became known that radon would concentrate in the light natural gas liquids. Radon has a boiling point intermediate between the boiling points of ethane and propane/propylene. As the natural gas liquids are separated from the natural gas, e.g., cryogenically, the radon is removed with the liquids and concentrates in the ethane and propane fractions.

In 1971, Phillips Petroleum Company was notified that propylene being sold to a customer was contaminated with high concentrations of radon. The radon content of the propylene was sufficiently high to interfere with the operation of instruments for determining the level of liquids in a propylene polymerization plant. The radon contamination was quickly recognized as an industry problem and not only a Phillips problem. After assuring that its employees were working in a safe environment, Phillips made presentations on the radon contamination to the major petroleum companies. The American Petroleum Institute, Phillips major customers for its natural gas liquids, and various state agencies were also notified.

The decay products of radon, lead-210 and polonium-210, contaminate most of the natural gas industry, especially the gas processing plants where the natural gas liquids are removed. Any equipment, vessels, tanks, pumps, etc. in contact with liquid ethane and propane are potentially contaminated with radon decay products. Gas

pipeline sludges can be contaminated also. One of the highest radiation readings I have seen in the industry was from a propane pump in a gas processing plant. The pump had a radiation reading of 25 millirem per hour! Propane pumps will usually be the most contaminated piece of equipment in a natural gas liquids facility. The decay products of radon contaminate sludges and form films on the interior surfaces of equipment, tanks and vessels.

Although natural gas may contain radon, the radon in the natural gas usually does not present a health hazard to employees or the public. Radon has a short half-life of 3.8 days, and is essentially gone in 30 days. Even when the gas or propane is used as a fuel before the radon has completely decayed, it has been shown that radon is not a major health hazard During the combustion process the radon is diluted by several volumes of air and is usually exhausted through the stack with the combustion products. Even when unvented, the carbon dioxide from the combustion is more hazardous than the radon.

The radon in the gas or gas liquids is not a major hazard to industry workers as long as it is contained inside piping and other equipment and vessels. The radon decay products can be a hazard, particularly to maintenance and other employees exposed to the interior of the equipment, vessels, etc. in the facility. The radiations from the decay products are too weak to penetrate the walls of the equipment, and do not present an external gamma radiation hazard.

Extent of NORM Contamination

The petroleum industry is only one of several industries that has NORM contamination problems. In fact, the mineral mining and processing industry, the phosphogypsum industry, and coal fired power plants generate more NORM wastes annually than does the petroleum industry. NORM contamination is possible at every petroleum facility. Although much of the NORM contamination can be minor, NORM contamination in production tubing scale has been seen in concentrations up to 430,000 pCi/gram in the North Sea and up to 160,000 pCi/gram in Michigan. Radium contamination in scale is very common at levels of thousands to tens of thousands of pCi/gram. Because of the wide distribution of uranium and thorium in the Earth's crust, radium contamination of all scale is probable. Much of this contamination may be very low, even less than the regulatory exempt level, but probably measurable by sensitive laboratory instrumentation. It has been estimated that 5 to 10% of pipe scale contains NORM

contamination in excess of regulatory levels.

It is difficult, if not impossible, to predict where NORM contamination will occur. Wells producing from the same field, for example, may have very different contaminated scale problems. Attempts to correlate NORM contamination with geological features have been largely inconclusive. The only way to determine if NORM is a problem is by a radiation survey of the well site or other facility. Although there are no accurate figures on the annual 'production' of NORM contaminated wastes in the industry, estimates run as high as several hundred thousand tons per year.

Exposure to NORM Contamination

Humans can be exposed to NORM radiation along many different pathways. Populations at risk from exposure to NORM radiation include workers at equipment cleaning facilities, such as pipe descaling operations, oil field workers, particularly in maintenance and repair operations, workers at facilities where NORM is disposed, and the public. The pathways of concern for occupational exposure include external gamma exposure, dust inhalation, skin beta exposure, radon/radon progeny inhalation and NORM contamination of bleeding or open wound injuries directly into the blood stream.

The Environmental Protection Agency believes radon emanation from radium NORM is one of the most hazardous features of NORM contamination, particularly as the radon may increase the radon levels in nearby structures. There is little radiation risk to oil field workers as long as the NORM contamination remains within the tubing, equipment, etc. When production tubulars are left in place in the ground, for example, there will be no exposure unless the contaminated material is brought to the surface. However, when the tubing is pulled, there can possibly be some external radiation exposure to workers due to the radium contaminating the scale in the tubing. The gamma radiation from the radioactive decay of radium is sufficiently energetic to penetrate the walls of the tubing. However, the dose rate within the tubing will be higher than that measured outside by a factor of at least five and possibly much higher. The difference in the dose rates is due to the shielding effect of the vessel walls. This can be of significance in pipe cleaning operations. The scale removed from the pipe can have 5 to 10 times the radiation dose compared with the radiation dose from the pipe before descaling.

Pipe cleaning yards tend to accumulate contaminated materials

through routine operations, thereby increasing the potential exposure of workers to radioactive dust, external gamma radiation, and elevated concentrations of radon. Soils near pipe cleaning facilities also may become contaminated by NORM, and may emanate appreciable quantities of radon that can cause an increase in the indoor radon levels in nearby structures.

The radon emanation rate from scale may be as low as 2 to 5%, but when broken into smaller pieces during scale removal, the radon emanation rate can be significantly higher. Opportunities for handling large amounts of scale that can contaminate entire facilities (equipment and soil) are common. The radium scale produced by pipe cleaning operations is one of the most pervasive environmental contaminants from present and past operations. As the radon from the decay of radium undergoes radioactive decay, the radon decay products may adhere to dust particles, further elevating the inhalation dose to workers and to any public in the vicinity.

Besides the potential for external radiation exposure and exposure to elevated concentrations of radon in the air, descaling operations may result in internal radiation doses if particles or dust containing radioactive materials are inhaled or ingested. During pipe descaling by rattling, a process by which a high speed rotating device in inserted into the pipe to break up and loosen the scale that is then blown out of the pipe with air, significant volumes of waste materials are formed. This process generates large quantities of dust that may be contaminated with NORM, and potentially increasing inhalation doses of radioactive material. Descaling by drilling or reaming also may produce quantities of radioactive dust.

Although the gamma radiation exposure associated with NORM is generally low, the decay of radium is accompanied by significant alpha particle emission. Alpha contamination is a major concern to personnel when ingested or inhaled. Dust inhalation and personal contamination can occur whenever contaminated scale and sludge are uncontained, but the risk is particularly great when repair and maintenance operations release airborne particles of NORM.

Risk to workers and the public is increased when NORM-contaminated materials are not properly disposed of and workers and the public may be exposed to external gamma radiation, the radon emanating from the NORM and from NORM-contaminated airborne dust. The improper disposal of NORM may contaminate soil and water and lead to higher concentrations of radon in the air in the vicinity.

Radiation exposure to workers and the public from NORM can

occur through at least eight different pathways:

1. Radon inhalation
2. Exposure to external gamma radiation
3. Groundwater ingestion
4. Surface water ingestion
5. Dust inhalation
6. Food ingestion
7. Skin beta exposure
8. Open wounds

Only when all potential pathways are evaluated can total doses be determined and the risk to workers and the public evaluated. Such a thorough evaluation can be difficult. Radon from the radioactive decay of radium may be the most significant contributor to exposures to the public from cleaning activities and NORM disposal. Improper disposal of NORM scale and other NORM wastes may lead to soil and water contamination, to direct exposure to individuals working or located nearby, and to higher indoor radon levels of nearby buildings.

Exposure to Radon

Radon, one of the earliest known radionuclides, has been the subject of increasing scientific and regulatory interest as the extent and implications of human exposure to radon and its decay products are more fully appreciated. A naturally occurring noble gas, radon pervades the human environment, and is one of the few environmental agents definitely shown to be a human carcinogen. Unusually high incidences of fatal pulmonary disease in uranium miners were noted as early as the sixteenth century (G. Agricola, 1597) and subsequent investigations of European and North American miners have established the link between bronchial carcinomas and elevated concentrations of radon and radon decay products. According to recent estimates, the largest radiological health burden associated with the release of radioactive materials is the radon gas released during the mining and milling of uranium, particularly from uranium tailing piles, and other industries, for example, petroleum, phosphogypsum, metal mining, etc. (EPA 1993). The production and processing of oil and natural gas liberates large quantities of radon that would have otherwise remained and decayed harmlessly underground.

Radon and radon decay product contamination in the natural gas-natural gas liquids industries are potentially as serious to these industries as the radium scale is in the oil industry. Because the radon is removed from the natural gas with the gas liquids, natural gas processing

plants are particularly susceptible to NORM contamination with the radon decay products, lead-210 and polonium-210. Although lead-210 is not a major health concern, polonium-210 is an alpha emitter with radiation properties similar to radium-226.

The significance of these and other chronic, low-level exposures is linked to the assumption that the dose-response relationship observed at high radon exposure levels can be reliably extrapolated down to lower levels. The currently prevailing assumption among regulatory bodies is that the dose-response relationship observed at high doses should be extrapolated linearly down to zero dose (National Academy of Science, 1972). Whether this assumption reflects reality, it remains true that the radiation dose burden due to radon and its decay products exceeds doses due to many other nuclides that have received considerably more scientific and regulatory attention.

Disposal of NORM Wastes

Before Louisiana developed NORM regulations, all scale generated in the oil and gas industry was disposed of without special precautions being taken. The disposal of NORM wastes presents a very difficult problem. Very few options are available, particularly cost effective options with present disposal costs varying from a few hundred dollars a barrel of NORM wastes to several thousand dollars a barrel. The EPA and various states are developing disposal options. Currently, one of the better methods, both technically and environmentally safe, is disposal of NORM downhole in a plugged and abandoned well or injected into an underground formation. Permits for such disposal are granted on a case-by-case basis.

The disposal options under consideration include:

- Abandoning contaminated production tubing in place.
- Disposal in plugged and abandoned (P & A) wells.
- Injection into a hydraulically fractured formation.
- Disposal in a licensed NORM waste disposal site such as Envirocare of Utah or US Ecology in Hanford, Washington.
- Release to a smelter for recycling.
- Land spreading and burial.

The preferred disposal method for NORM wastes is the one that adequately protects the environment at the lowest cost to the operator. Regulatory constraints often limit the options of the operator to methods that may not be necessary for environmental protection.

Regulation of NORM Contamination

The International Commission on Radiological Protection (ICRP) recently recommended lowering the allowable occupational level of exposure to ionizing radiation from 5 rem/year to 2 rem/year. However, in the recent revision of 10 CFR 20, the allowable level for radiation workers was kept at 5 rem/year. The ICRP recommended and 10 CFR 20 concurred in lowering the dose limit for the public from 500 mrem/year to 100 mrem/year. Typical oil field workers or personnel in a pipe descaling facility are classified as members of the public and are limited to 100 mrem/year. To be classified as a radiation worker and subject to the higher exposure limits requires that the worker be trained in radiation safety and wear a personal radiation monitoring device. Radiation dose rates from some contaminated equipment, e.g., contaminated scale removed from production tubing, can be sufficiently high to cause a worker near the tubing, to receive an annual dose from ionizing radiation greater than the allowable level.

Because of the perceived hazards of NORM exposure, state and federal agencies are drafting specific regulations for the control of NORM. Four states, Louisiana, Texas, Mississippi and Arkansas, have regulations for the control of NORM enacted, several other states will enact regulations in 1994, and the EPA, responding to increasing public pressure for environmental controls and the public's emotional fear of radiation, will possibly have NORM regulations later this year, particularly for contaminated site cleanup. Regulations developed for radioactive scale probably will set the pattern for regulatory requirements for other radioactive solids, such as tank sludges, pigging wastes, gas processing wastes, etc.

Of particular interest to the industry are the parts of the regulations that exempt small concentrations of NORM, and provide guidance and regulations for the release of facilities for unrestricted use.

These regulations will supplement general regulations already in place for the control of radiation at the state and federal levels. The petroleum industry is required to be in compliance with the general regulations as well as the specific NORM regulations now being promulgated. For example, the general radiation regulations specify

rules for monitoring airborne radioactivity, posting of radiation areas, worker protection and training requirements and informing employees of the potential radiation hazards.

Management and Control of NORM

Basic knowledge of the environmental laws and regulations is necessary for the design, construction, and operation of oil and gas facilities if a project is to be successful and if costs are to be minimized. Environmental management must be integrated into operational decisions to minimize future (hidden) liabilities.

The key to a NORM management program is a survey of the facility to determine if NORM is present. If found, a program for its control must be developed, i.e., a program that provides for the safety of the employees, and the protection of the environment and the public. As a minimum, management control programs should:

- Include radiation surveys to determine areas of NORM contamination.
- Establish programs to ensure employee safety and protection of the environment.
- Inform facility personnel of the potential hazardous contamination.
- Establish procedures for the disposal of NORM wastes.
- Review applicable federal and state regulations to ensure compliance.

Litigation

Any waste generation or discharge of contaminants into the environment has the potential for future liability. Environmental management programs reduce the potential for undesirable surprises and minimize this hidden liability. These environmental programs consist of assessments, waste minimization, record keeping, documentation, and up-to-date training.

Litigation involving real or perceived exposures to NORM is increasing, with major lawsuits in Mississippi, Louisiana, and Kentucky involving personal injury and property damage. The emotional fear of radiation and radioactivity will certainly be a factor in NORM litigation. It is important for the industry to begin developing its defense against such litigation that is certain to accelerate in the future. Detailed documentation of NORM surveys and other control measures are necessary as well as close compliance with NORM and general radiation regulations from the federal and state governments. Although few states have yet enacted specific regulations for the control of NORM, facilities in the regulated and non-regulated states should begin documenting their NORM contamination problems.

Conclusions

- NORM contamination is potentially possible at every petroleum facility.
- The presence of NORM in oil and gas production facilities, gas processing plants, pipelines, and other petroleum equipment and facilities, is not, in general, a serious technical problem, but can be a serious public relations problem.
- The concentrations of NORM contamination are generally low and do not normally present a health hazard to the public or to most persnnel in the industry. Some facilities may be more highly contaminated, however, and may be hazardous, especially to maintenance, cleaning, and disposal personnel.
- Radium contamination of pipe scale can be a serious problem requiring special procedures for the removal and disposal of contaminated scale to prevent contamination of personnel and the environment.
- Produced water may be contaminated with radium, requiring special procedures for the protection of the environment.
- Surface equipment and facilities at production sites may also be contaminated with NORM, requiring special repair and maintenance procedures and the disposal of NORM

contaminated wastes.

- The buildup of long-lived radon decay products (specifically lead-210) in gas pipelines, gasoline plants and refineries requires that speciic procedures be implemented for inspection and maintenance personnel to ensure their safety when working on the internal parts of equipment and facilities where radon may have been present.

- A serious problem that must be addressed is the disposal of radioactive materials and equipment. Options available for the disposal of NORM and NORM wastes are presently limited.

- Although only Louisiana, Mississippi, Texas and Arkansas have enacted specific regulations for the control of NORM, other states will have regulations in 1994 and most petroleum states will have regulations within five years. The EPA is considering NORM regulations for the control of NORM on the federal level.

- The industry must comply with the NORM and other radiation regulations.

"Although potentially hazardous to personnel and the environment, NORM contamination is controllable."

"NORM contamination should be respected, but not feared."

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Geochemistry of Radium and Environmental Risk

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Human economic activities have modified global flows of radium (Ra) to near-earth-surface environments. In order of decreasing Ra flux, production of phosphate fertilizer, oil and gas production, coal mining and burning, and the uranium fuel cycle all contribute Ra to the environment. Anthropogenic Ra flows now account for approximately 10% of total Ra translocations in the near-earth-surface environment. The environmental behavior of Ra and the risk it poses to human populations cannot be divorced from the chemistry of the elements that both proceed and succeed it within natural uranium (U) and thorium (Th) radioactive decay-chains. The signal radiochemical event in these decay chains is the production of a noble gas, radon (Rn), which can readily migrate in the environment. This release of Rn appears to be the largest threat from the presence of Ra in the environment. In contrast, Ra, is a highly immobile element under earth-surface conditions. The chemical-transport behavior of Ra is dominated by its formation of a highly insoluble sulfate and its strong cation exchange properties. These chemical behaviors force Ra to be largely associated with inert solids in marine, aquatic, and terrestrial environments. As a consequence of these chemical behaviors, Radium is highly immobile in near-earth-surface environments. Although the biota in marine and aquatic systems bioconcentrate Ra, bioconcentration factors diminish with increasing trophic level. As a result, Ra does not become highly concentrated at high trophic levels in the food chain. In terrestrial systems, most plants discriminate against Ra uptake, and the efficiency of the translocation of Ra from plants to animal tissues is very low. In short, Ra,

as influenced by normal environmenal geochemistry, poses little threat to man. Threats to man that may accrue, however, derive from Rn exposure and possible inhalation of fine Ra-contaminated particles. These risks have not been fully addressed by current regulatory constraints on handling and processing naturally occurring radioactive materials.

Radiation Hazards

External radiation sources can pose a threat to human health, but this threat can be easily mitigated. When naturally occurring radionuclides spontaneously decay they emit ionizing radiation in the form of helium nuclei, electrons, and high energy photons (referred to as α, β, and γ radiation, respectively). Despite their high energies, the external radiation threat to human health posed by α and β emissions can be readily mitigated by modest shielding. The energy of α paticles is completely dissipated after traveling a few centimeters in air, and α particles cannot penetrate human skin. Although far more penetrating, β particles can be completely stopped by a thin aluminium sheet, and can penetrate only the surface layer of human skin. In contrast, γ radiation can penetrate thick steel, and can completely pass through the human body. This makes γ radiation the primary risk from an external radiation source.

Internal radiation sources pose a far greater risk to human health than external sources. Internal radiation sources, once in place, cannot be avoided. For the same degree of radioactivity, internal sources that emit α and β particles pose a greater health threat than γ emitting sources. This is because α and β particles deposit all their energy in tissues surrounding their source. The high energy photons comprising γ radiation do not interact as strongly with matter, and much of the energy from an internal γ source will pass harmlessly through the body.

Internal radiation sources derive from radioactive material that is either ingested or inhaled. After inhalation or ingestion, this radioactive material may remain as distinct foreign particles, or actually be metabolized and become incorporated in tissues. Depending on the physical and chemical nature of the inhaled or ingested material, it may or may not be be able to pass from the body. The most damaging internal source materials, then, are those which are α and β emitters whose chemistry or physical size allows more or less permanent association with biological tissues.

The foregoing is general description of risks to biological tissues associated with exposure to ionizing radiation. The reader is advised, however, that all radiation exposure (α, β, or γ), whether internal or external, contribute to

Geochemical behavior is largely determined by size and charge. In Fig . 2 atomic volume is plotted against atomic number. The resulting cyclic curve organizes siderophiles at minima, chalcophiles on curve sections of increasing atomic volume, with an atmophile element following, and lithophiles at maxima and decreasing curve sections. Although atomic volume appears to generally organize elemental behavior for gaseous and solid earth materials, both size and charge must be considered when examining geochemical commerce between elemental reservoirs at and near the earth's surface. Factors controlling elemental mobility in the near earth surface environment include strength of interaction with water, the energy required to displace or add electrons, and interactions with major dissolved and solid components. For metallic elements, interactions with major negatively charged oxyions (i.e., hydroxide (OH^-), carbonate (CO_3^{-2}), and sulfate (SO_4^{-2})), sulfide (S^{-2}), and anionic solids (e. g., clay minerals and organics) are very important mobility determinants.

Mobile metallic elements do not form low-solubility oxides, hydroxides, sulfates or sulfides, and tend to have only weak associations with anionic solids. This pattern is illustrated in Fig. 3 which diagrams the results of chemical weathering of a typical granitic rock. Silicon (Si) in the form of quartz , aluminium (Al) and iron (Fe) as clays and oxides remain behind as solids. Alkali and alkaline earth metals (Group I and Group II elements) are transported to the ocean. In the ocean, alkali metals remain in solution, whereas the alkaline earths are precipitated as carbonates and sulfates.

Natural Production and Occurrance of Radium

Radium is a polyisotopic element. Twenty-five Ra isotopes with mass numbers between 206 and 230 are known, but only four occur naturally (Weigel, 1977; Brown, Dairiki, and Doebler, 1978). These naturally occurring isotopes, ^{226}Ra, ^{228}Ra, ^{224}Ra, and ^{223}Ra, are all intermediate members of the three natural actinide element decay series (Fig. 4). All Ra isotopes occur in nature only because they are continually produced by long-lived parents. Even the longest lived isotope, ^{226}Ra, has a geologically brief half-life (1599 yr). The half-lives of the other natural Ra isotopes are far shorter. As a consequence of its long half-life and the abundance of its long-lived parent, ^{238}U, the most important Ra isotope

absorbed dose. Once the absorbed does is large enough, adverse biological responses will occur.

Isotopes of Ra, and their decay daughters, especially Rn, can be viewed as high health hazard materials. Most of the energy released from the decay of Ra and its decay daughter products is via the emission of α particles. The chemistry of Ra is similar to that of calcium (Ca). Consequently, Ra can become incorporated in bone and other Ca-bearing tissues. When so incorporated, the radioactive decay of Ra and its daughter products exposes surrounding tissues to a high dose of ionizing radiation. Because it is a gas, Rn, if present in air, is inhaled. More importantly, Rn decay yields radioactive metallic ions which may become associated with fine particles. If sufficently fine, such particles may become lodged in deep lung tissue. In fact, inhalation of ^{222}Rn present in normal air is estimated to comprise the single largest radiation dose to the human population at large (Nero, 1989).

Geochemistry

The three main missions of geochemistry have been clearly stated by Clarke (1924) and Goldschmidt (1954) . First, geochemistry is concerned with determining relative and absolute abundances of elements and isotopes in the earth. Second, geochemistry aims to describe and explain the distribution of elements among various earth-system components (e.g., crust, hydrosphere, atmosphere). Third, geochemistry seeks to describe and explain the extent and nature of elemental commerce among earth system components. In recent years, a major thrust of geochemical investigations has been to document and explain anthropogenic impacts on chemical commerce in near-earth-surface environments.

Classically, the naturally occurring elements have been classified as siderophile, chalcophile, lithophile, or atmophile for, respectively, strongest association with metallic iron, sulfides, silicates, or the atmosphere. The periodic table from a geochemical perspective is given in Fig. 1. Atmophile elements are all gaseous. Lithophiles are those that readily form ions with an outermost 8-electron shell. Chalcophiles are members of the B subgroups, whose ions have 18 electrons in their outer shells. Siderophiles are those of Group VIII and some neighboring elements with incompletely filled outer electron shells.

in nature is ^{226}Ra. Significant nuclear and chemical properties of the four naturally occurring Ra isotopes are given in Table I. Except for ^{228}Ra, all of these isotopes decay via modestly energetic (~5 MeV) α emissions to yield a Rn isotope. In this process, relatively low energy γ photons (0.1 to 0.4 MeV) are also emitted. The exception, ^{228}Ra, decays via a β emission to ^{238}Ac then, via β emission to ^{228}Th, and finally via α emission to ^{224}Ra.

Since Ra is formed by the decay of U and Th isotopes, its distribution in earth materials is, to a first approximation, dependent on the distribution of U and Th bearing minerals. Even so, observed ratios of ^{226}Ra / ^{238}U (and ratios of ^{224}Ra, ^{228}Ra / ^{232}Th) show deviations from secular equlibrium. This indicates that, as would be expected, Ra has distinctly different geochemcal behavior from its long-lived parents and, thus travels through the environment via distinctly different pathways.

Because U and Th are widely distributed in the earth's crust, Ra is also widely distributed. Table II provides a summary of data concerning ^{226}Ra abundance in various rock types. As can be readily observed, ^{226}Ra is more abundant in silica-rich igneous rocks than in silica-poor rocks. Among igneous rocks, ^{226}Ra is more abundant in acidic rocks than in basic or ultrabasic rocks. Clay-rich, organic-rich, and phosphate-rich sedimentary rocks have far greater levels of ^{226}Ra than carbonate rocks which, in turn, are richer in ^{226}Ra than typical sandstones.

In normal uncontaminated soils, the abundance of ^{226}Ra appears to be controlled by the abundance of U and Th, and reported ^{226}Ra activites in these soils shows a broad range (0.1 to 3.4 pCi/g) (Frissel and Koster, 1990; Iyengar, 1990). Soils associated with Th-rich monazite can contain 1000 pCi/g ^{226}Ra (Khademi, Alemi, and Nasseri, 1980), and under other special circumstances (a soil derived from highly weathered limestone associated with volcanic ash) levels of ^{226}Ra in excess of 300 pCi/g have been observed in uncontaminated soils (Marsden, 1963).

Typically, surface waters on continents have very low levels of ^{226}Ra activity. The estimated mean global value for rivers is approximately 0.07 pCi/L , but some drainage basins in North America, Europe, Asia, and Africa have levels much greater than this (up to 7.9 pCi/L in a Czechoslovakian river) (Iyengar,

1990). The reasons for such elevations in ^{226}Ra activity reflects either local geology or anthropogentic inputs. Groundwater typically contains more ^{226}Ra than surface water, and ^{226}Ra activities measured in groundwater are highly variable. Geothermal settings, or association with U, Th, or phosphate mineralization can yield very high levels of ^{226}Ra. In Finland, for example, well water from a U and Th-rich granite has been measured at just over 255 pCi/L ^{226}Ra activity (Asikainen and Kahlos, 1979).

Reported ^{226}Ra activity is low in all of the seawater data reviewed by Iyengar (1990). This is as expected due to the high SO_4^{-2} content of seawater. The highest value reported for seawater was just under 1.5 pCi/L. The general trend observed is for ^{226}Ra activity to increase with increasing water depth in the open ocean (increasing from about 0.03 pCi/L in surface waters to about 0.1 pCi/L in deep waters). The apparent removal of Ra from surface seawater has been attributed to its association with siliceous organisms which, when they die and fall to the bottom, are known to scrub Ba from surface seawater. Coastal seawater ^{226}Ra activities are higher than open ocean surface activities, and are comparable to those observed for deep oceanic water.

Observations of normal groundwater, surface water, and seawater suggest that Ra is less mobile than U. Typically, the Ra/U ratio of these fluids indicates a deficiency of Ra. This is not true for high-salinity, deep, subsurface waters produced with hydrocarbons. These waters can be highly enriched in Ra with respect to U, and the isotopic composition of the Ra indicates a variety of parental (i.e., U and Th) compositions for the Ra sources (Bobin, 1933; Komlev, 1933; Nikitin, 1933; Gott and Hill, 1953; Pierce, Mytton, and Gott, 1955; Armburst and Kuroda, 1956; Kraemer and Reid, 1984; Kramer, 1981; 1985; 1986a; 1986b). Ostensibly, the high concentrations of Ra observed for produced water is is due to the extremely high total salinity of these waters, their low SO_4^{-2} content, and high chloride content. Such waters may enhance the solubilization of Ra by virtue of inhibited ion exchange with clays, the lack of a low solubility precipitate, and, possibly, the formation of a Ra-Cl ion pair (Kraemer and Reid, 1984). Some workers have suggested that the abundance of Ra in hydrocarbon associated waters is the result of enhanced Ra soubilization by unknown and unidentified organic-inorganic interactions (Filonov, 1964; Gutsalo 1964, 1967). Indeed, Gutsalo (1967) shows a fairly convinincing correlation between Ra abundance and

the quantity of hydrocarbon gas dissolved in subsurface waters in the Dnieper-Donets basin. For the Gulf Coast, available data show a clear correlation with salinity for high-salinity (NaCl waters). Shown in Fig. 5 is a plot of Ra abundances in produced waters as a function of salinity. The four data sets (onshore Gulf Coast, U. S. (Kramer and Reid, 1984), offshore Western Gulf of Mexico (unpublished Amoco data), Delaware Basin, eastern New Mexico (Herczeg, *et al.* 1988) and the Dnieper-Donets basin (Gutsalo, 1964), show a decided correlation of Ra concentration and salinity. The data from the Dnieper-Donets basin waters , however, do have higher Ra abundance than would be predicted by the Gulf Coast data , and data from the Delaware basin exhibit some high Ra concentrations at fairly low salinities.

Radium Geochemistry and Geochemical Cycling

From the above discussion, it is clear that an evaluation of the environmental geochemistry of Ra cannot be divorced from the chemistry of its precursor and successor elements in the decay chains that produce it. The decay chains that produce Ra progress from lithophile elements to an atmophile element, and finally to chalcophile elements. As a consequence, chemical transport paths for decay products in U and Th decay-series show ever increasing divergence with each subsequent decay.

Radium itself is an alkaline earth metal (Group IIA). The radiological significance of Ra is its incorporation in bony tissues. The chemical behavior of Ra is relatively simple. Only one oxidation state (+2) is known. It is a lithophilic element. It does not form minerals of its own. The atomic and ionic size of Ra are nearly equivalent to those of Ba. Consequently, its geochemical behavior is much like that of Ba. The key chemical characteristics of Ra in geologic settings of environmental interest (e.g., surface water, groundwater, seawater, soils, and sediments) are its formation of highly insoluble sulfates and carbonates, lack of strong association with common natural ion pairing agents, and very strong binding by anionic solids. In short, Ra would not be expected to be a particularly mobile element in most near-earth-surface environments. Under oxidizing conditions in the presence of sulfate, it is coprecipitated with Ba as a sulfate. In

the presence of clays or organic matter Ra is strongly associated with these anionic solids through cation exchange.

Detailed data on the total mass and radionuclide inventory (i.e., U, ^{226}Ra, Th, ^{228}Ra) of major earth system components, and fluxes of ^{226}Ra among these reservoirs are given in Table III. Transfer of Ra among major earth-surface components is shown as a compartment and flux model in Fig. 6. The largest Ra reservoir is the crust. Chemical and physical weathering of the crust (along with anthropogenic disturbances) transfers Ra into oceans, soils, groundwaters, glaciers, freshwater lakes and rivers, the biosphere, and the atmosphere (in decreasing order of ^{226}Ra inventory). These processes disperse Ra in the environment, and, in some cases are responsible for its enrichment in some components of the biosphere.

Although the global inventory of Ra is, necessairly, at secular equlibrium with parental U and Th isotopes, this is clearly not the case in a local sense. The existence of radiodisequlibria are, in fact, direct evidence that Ra moves differentially from U and Th in the environment.

The crust, as a whole, is at secular equlibrium. This is not suprising because most of the crust is inaccessible to weathering and transporting fluids. The world ocean, however, is decidely not at secular equlibrium. The ocean as a whole is seeing Ra removal in excess of its supply from erosion of crustal materials and *in situ* production via the decay of U and Th. It should be noted that the time scales for supply and removal for ^{226}Ra and ^{228}Ra are vastly different due to the great difference in their half-lives. It appears that secular equlibrium does exist between ^{232}Th and ^{228}Ra in the world ocean and clearly does not exist for ^{238}U and ^{226}Ra. Soils clearly show an excess of Ra with respect both U and Th decay chains. This indicates an obvious disequlibria. The cause(s) for the disequlibria in soils could be rapid leaching of U and Th with respect to the leaching of Ra during weathering or an exogenous supply of Ra to soils. Given the short half-life of ^{228}Ra and the long half-life of ^{232}Th, it would appear that the cause of Ra enrichment of soil is not purely weathering. Groundwater, as a whole, is at secular equlibrium. This is probably a reflection of the long residence time of most groundwaters in the near-surface crust. Glacial ice is decidedly not at secular equlibrium, and shows an enrichment in Ra similar to that in soil. This is not a

suprising result, because the main source of tropospheric particulates is continental dust. The biosphere contains a significant inventory of ^{226}Ra and ^{228}Ra, both of which are substantially out of equlibrium with their parents. The disequlibrium with respect to ^{228}Ra suggests a strong preference for Ra over either U or Th. This is not suprising in that Ca is an important structural and physiological element in both plants and animals; some uptake of Ra is unavoidable. The atmosphere contains a small inventory of Ra which has approximately the same disequlibrium status as soil and glacial ice. Since the residence time of particulates in the atmosphere is comparable to that of water (~10 days) (Garrels, Mackenzie, and Hunt, 1975) it is suprising that a Ra inventory exists at all. This atmospheric inventory of Ra coupled with a 10 day residence time would predict a equlibrium flux rate of ~3900 Ci ^{226}Ra / yr. This is a fantastically large number, considering that it represents just under a third of the total inventory of ^{226}Ra estimated for the biosphere. Even so, it is comparable to the equlibrium atmospheric flux rate for ^{226}Ra estimated from detailed measurements of glacial ice (~ 6500 Ci ^{226}Ra / yr).

Given in Table II are estimates of annual ^{226}Ra flows. No global estimate for the total flow of ^{226}Ra to near-earth-surface environments as a consequence of hydrocarbon production has been published. Indeed, data to arrive at an accurate estimate are lacking. Even so, an approximation of annual ^{226}Ra flow due to hydrocarbon production can be constructed from a consideration of world oil production and the existing estimate for ^{226}Ra present in hydrocarbon-associated solid wastes (pipe scales and sludges) for the United States (EPA/SCA, 1991). The EPA estimate of diffuse NORM (naturally occurring radioactive materials) generated by petroleum operations in the United States is 456×10^3 tons / yr (413.7×10^9 g). These solid wastes are estimated to have a mean ^{226}Ra activity of ~155 pCi/g. This translates to ~64 Ci of ^{226}Ra in hydrocarbon-associated solid wastes produced in the United States in 1991. Assuming that this scales globally, an estimate of worldwide hydrocarbon associated ^{226}Ra production can be made based on global hydrocarbon liquids production (gas production was not included in this calculation because most water production is associated with hydrocarbon liquids rather than gas). The estimate ratios of U.S. hydrocarbon liquids production to global hydrocarbon liquids production are 7.1 (1989 data, Banfield, 1990), 7.5 (1991 data; Meyer, 1993), and 7.9 (1991 data; API, 1993) . Given these ratios, and assuming the same average ^{226}Ra activity as

that published by EPA , the global production of ^{226}Ra in hydrocarbon-associated solid wastes is between 454 and 505 Ci (average = 480 Ci). For the moment, this is assumed to be a ^{226}Ra flow to soils; much of the low-level NORM waste is disposed of in landfarms (a method of waste treatment by land application -- not an agricultural activity). This does not, of course, account for ^{226}Ra discharged to the ocean as a consequence of offshore oil and gas production, and an estimate of this ^{226}Ra flow is more difficult. Little hard data exist concerning the total volume of water produced with hydrocarbons globally, the average ^{226}Ra activity of global produced water (generally saline water co-produced with hydrocarbons) is unknown, and the fraction of produced water discharged to the oceans is unknown. Nonetheless, it is worthwhile attempting an estimate of ^{226}Ra flow to the ocean. As constructed here, this estimate is conservative. If we assume a 10:1 (v:v) water:oil ratio for produced fluids and a median ^{226}Ra activity of 235 pCi/L based on the references cited in Fig. 5, and worldwide oil production estimates by API (1993), worldwide hydrocarbon associated water production is estimated at ~215 x 10^9 bbl (based on the 10:1 v:v water to oil ratio assumed, this is judged to be an overestimate). Not all of this water is discharged to the environment. Typically, onshore hydrocarbon production operations re-inject produced water. Consequently, only offshore produced water is considered to constitute a ^{226}Ra flow to the world ocean. Based on API (1993) data, the average ratio (for the period 1990 - 1992) of total oil production to offshore oil production is ~16:1, consequently only 13.5 x 10^9 bbl of produced water is discharged to the world ocean. This constitutes a flow of ~543 Ci of ^{226}Ra to the ocean.

Four key points can be made with these data. First, anthropogenic flows are not insubstantial. In all, human activities are responsible for ~ 2750 Ci /yr of ^{226}Ra flux to the environment (~10% of all ^{226}Ra flow) (see Fig. 6). Second, the single largest anthropogenic ^{226}Ra flow derives from the application of phosphate fertilizersto enhance agricultural yields (Jaworowski, 1990a). The Ra in phosphate fertilizers arises as a consequence of the association of elevated U levels in natural phosphate rocks (Guimond, 1990). This single flow is ~ 1100 Ci of ^{226}Ra each year and is squarely directed at soils used to produce food! Third, the sum of ^{226}Ra fluxes due to the production of energy from coal and nuclear sources is ~226 Ci / yr. Fourth, the estimate of ^{226}Ra flux due to hydrocarbon production developed above suggests that this source of ^{226}Ra is, in a global sense, approximately equivalent to that from worldwide phosphate fertilizer

production. This is, however, an unfair comparison given that ^{226}Ra in oil and gas solid wastes is either disposed of as solid waste and not applied directly to agricultural land. It is fair to state, however, that man's greatest impact on the global budget of ^{226}Ra derives from man's two greatest needs: food and fuel.

Radon Geochemistry

The direct decay daughter of ^{226}Ra is ^{222}Rn. Radon is a noble gas, and, as a result, is not chemically reactive. It is relatively soluble in water (230 cm^3 kg^{-1}), and modestly soluble in oil (~9.2 cm^3kg^{-1} based on its solubility in paraffin oil). By virture of its large size, it can be readily absorbed by charcoal, silica gel, and similar substaces. Significant chemical and radiochemical attributes of Rn are given in Table III. The migration of Rn from solids into surrounding air is not easy to predict. This is because the movement of Rn is governed not only by the complex of physical factors which control the movement of materials through porous media , but also by its ability (or lack thereof) to escape from a solid once produced (i.e., emanation efficiency). Despite the well known strong binding of Rn by activated charcoal and similar materials, no studies of Rn movement through soils and sediments have clearly addressed the effects of soil organic matter on Rn migration. Data recently obtained by Amoco indicate that the presence of a relatively small amount of activated charcoal in a simulated NORM pipe-scale contaminated soil greatly reduced the net Rn emission from the soil. The data shown in Fig. 7 show that even the addition of a modest amount of activated charcoal to a NORM pipe-scale contaminated soil greatly reduces Rn emanation.

Radon is important radiologically because, as a gas, it has the potential of introducing U and Th decay products into the air humans breath. A link between Rn exposure and lung cancer risk has been highly publicized . Literally millions of Rn assays have been conducted for indoor air in the United States and elsewhere. The evidence for a direct link between Rn exposure and lung cancer is, however, ambiguous (Mills, 1990). Such a link may well exist, but its nature is clouded by the fact that decay product exposures act to some degree synergistically with cigarette smoke and other fine aerosols, such as rock flour (National Research Council, 1988). The significance of the synergism is the association of Rn decay products with fine airborne particles (see Fig. 8).

The chemistry of decay daughters shifts radically when Rn decays. Decay

daughters subsequent to Rn are Po, Pb, Bi, and Tl isotopes. For ^{226}Ra decay, the chemically significant product in this phase of the decay chain is ^{210}Pb. Lead is a siderophile element. In sediments it is likely to be immobilized as a sulfide. In soils it is most likely present as an insoluble carbonate, but due to its chemical similarity to Ca, may be present as an exchangeable cation. In addition, Pb is a volatile element, materials that contain Pb, when heated may release Pb as a vapor. The radiological significance of ^{210}Pb derives from its relatively long half-life (22 years), the likely location in the body (the lung), and the notable recalcitrance of Pb to excretion once ingested.

Radium in Organisms

As shown earlier (Fig.6), Ra is incorporated by both plants and animals in aquatic, marine, and terrestrial environments. An enormous literature exists concerning Ra uptake by biota. This literature has been thoroughly reviewed in recent publications of the International Atomic Energy Agency (1990). In overview, the conclusion that can be drawn from this body of information is that although Ra is taken up by both plants and animals it has a very poor transfer efficiency across trophic levels. Under normal environmental geochemical conditions, Ra is not substantially bioconcentrated in soft animal tissues.

Marine algae, zooplankton, molluscs, crustaceans, and fish incorporate radium from seawater into their tissues and concentrate it to varying degrees (concentration factors varying from ~10 to ~10^3; (Bonnoto, 1990; Iyengar and Rao, 1990). In general, orgamisms at lower trophic-levels, such as phytoplankton, concentrate radium from seawater to a higher degree than organisms at higher trophic-levels (e.g. fish). This poor migration of Ra through the marine food chain. In addition, as would be expected, hard, calcified biological materials (shell, bone, and chitin) are relatively richer in Ra than soft tissues (Iyengar and Rao, 1990).

In freshwater systems, planktonic and attached algae can accumulate Ra from water, and rooted macrophytes appear to be able to extract it from sediments. Observed concentration factors for both macrophytes and algae are small (~10) for algae, and for macrophyte accumulating Ra from water <<1 (0.014) (Williams, 1990). Freshwater sponges, molluscs (both gastropods and bivalves), arthropods

(both crustaceans and insects), and fish can take up Ra from their environment (Jeffree, 1990; Justyn and Havlik, 1990). Uptake of Ra by aquatic animals depends on many factors including age, diet, nutritional status, levels of other alkaline earth metals, and sex. As with marine animals, Ra varies among tissues, but tends to be concentrated in hard calcium-rich biological materials. Concentration factors (with respect to water) for freshwater fish are comparable to those of marine fish (~ 1-5 x 10^2).

Simon and Ibrahim (1990) provide an excellent review of interaction between plants and Ra. In general, terrestrial plants actively discriminate against incorporating Ra in their tissues. Terrestrial plants typically have bioconcentration factors << 1.0. An interesting exception to this overall behavior is the Brazil nut tree which notably concentrates Ra (~100 x soil concentrations) in its nut (i.e. endosperm) and to lesser but significantly large factors in other tissues. Interestingly, plants growing in soils with notably high Ra activities (both natural soils and uranium mill tailings) do not exhibit greater uptake, proportionally, than similar plants in normal soils. In fact, one of the suprising aspects of investigations of Ra uptake by terrestrial plants is the finding that bioconcentration factors can decrease exponentially with increasing Ra concentration.

Lastly, terrestrial primary consumers do not appear to easily transfer Ra to their soft tissues in normal environmental settings (Halbert, *et al.*, 1990). The fraction of Ra contained in food and water consumed by domestic animals that can be transferred to tissues used as food by humans is quite small (~ 10^{-3} maximum and typically ~ 10^{-4}).

Radium and Environmental Risk

The real issue surrounding Ra in the environment is the risk it does, or does not, pose to man. More significant than the presence of a potential radiation source is the availability of an exposure pathway. Although it is beyond the scope of this paper to provide a rigorous environmental assessment model for radiation exposure due to Ra present in NORM oil-field wastes, it is within the scope of this paper to examine the geochemistry and biogeochemistry of Ra explored here to develop a heuristic model of the risk of radiation exposure from Ra in oil-field NORM. A schematic diagram showing a generic suite of pathways for the transport of contaminants from a source to humans is shown in Fig 9.

Both internal and external exposures may accrue from the presence of a Ra source. The external threat from Ra is real, but can be readily mitigated by covering contaminated soil with uncontaminated material (Wilson and Scott, 1992). Because of the relatively high atomic number of Ca, oyster shells or crushed limestone would provide better shielding for a smaller thickness than silicate rich materials.

A cursory examination of this diagram indicates that if a contaminant cannot enter groundwater, surface water, soil, or air it cannot pose an internal exposure threat to humans. As has been clearly shown in the literature reviewed here and elsewhere, Ra is simply not a particularly mobile element under near earth surface conditions. Translocation of Ra from a solid, low solubility, sulfate salt to groundwater or surface water will happen very slowly (if at all). The overwhelming conclusion from numerous studies of ^{226}Ra movement away from uranium mine tailings (some mine tailings in excess of 40 years old) is that Ra does not really migrate through soil to groundwater (see the extensive review given in Frissel and Koster, 1990). In fairness, Ra has been observed to disperse away from areas of concentration, but this dispersion appears to be the consequence of physical transport of fine particles from the phosphate fertilizer process waste by sheet wash rather than in solution (Paul and Pillai, 1990).

Transfer of Ra by ingestion of animal and plant tissues is an unlikely route for human radium exposure. Within aquatic, marine, and terrestrial food webs, the overwhelming weight of evidence shows that Ra is not readily passed to higher trophic levels. Although aquatic and marine plants may bioconcentrate Ra it shows increasingly lower bioconcentration factors with increasing trophic level. In terrestrial systems, primary producers do not concentrate Ra from soil, and the fraction transferred from water and feed to human foodstuffs is vanishingly small. Lastly, the transfer of Ra from foodstuffs to humans largely depends on using a Ra contaminated site for production agriculture.

Transfer of Ra to humans via inhalation of particulates or by ingestion following deposition of contaminated particles on land used for production agriculture is a clear potential Ra-exposure pathway. Even so, no specific studies exist that examine the issue of transfer of Ra-containing particulates from

contaminated soils in pipe yards or particulates generated during pipe and equipment cleaning operations to the human lung. In view of the fact that Ra-containing wastes are now being concentrated at centralized points for processing, this is an obvious research need. Are NORM processing facilities releasing harmful particulates to the communities that surround them? Could contaminated particulates dispersed from NORM processing facilities contaminate agricultural products?

Exposure to Rn and its decay daughters is another obvious exposure pathway that should be considered. Indeed, studies of U mill tailings (see review by Halbert, *et al.* 1990) have shown that the single largest radiation exposure is by way of inhalation of Rn and its decay daughters. In the NORM arena, we do not have a large group of measurements of Rn emanation coefficients for contaminated soils. Further, no published information exists concerning the Rn emanation power of hydrocarbon production scales and sludges, and no published information exits concerning the Rn environment of centralized NORM processing facilities, or the Rn fluxes that might be expected from such facilities to the environment at large.

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Table I. Chemical Characteristics and Behavior of Radium

Radium **Ra**

Atomic Number 88
Relative Atomic Mass (C=12.00000) 226.0254
Discovered 1898 by P. Curie & M. Curie @ Paris

Crustal Abundance ~ $6x10^{-7}$ g/tonne				
Radii x 10^{-12} m	Atomic = 223	Crystal (Ra^{+2}) = 152		Hydrated = 398
Electronegatvity	Pauling = 0.89	Allred = 0.97	Absolute = na	
Standard Reduction Potentials		Ra^{+2} ☛ Ra^0		-2.196 V
		RaO ☛ Ra^0		-1.319 V
Electronic Ground State Configuraton $[Rn]7s^2$				
Oxidation States Ra^{II} ([Rn])		RaO_2, $Ra(OH)_2$, $[Ra(H2O)_x]^{+2}$ (aq), Ra^{+2} salts		
Melting Point ^0K	Boiling Point ^0K	ΔH_{fusion} kJ mol^{-1}	$\Delta H_{vaporization}$ kJ mol^{-1}	
973	1413	7.15	136.8	
Thermodynamic Properties		298.15^0 K, 0.1 MPa		
State	$\Delta_f H^\theta$ kJ mol^{-1}	$\Delta_f G^\theta$ kJ mol^{-1}	S^θ J K^{-1} mol^{-1}	C_p J K^{-1} mol^{-1}
Solid	0	0	71	27.1
Gas	159	130	176.47	20.79
Density kg m^{-3}	Thermal Conductivity W m^{-1} K^{-1}	Electrical Resistivity Ω m	Molar Volume cm^3	Coeff. Linear Thermal Expan. K^{-1}
~5000 @ 293^0 K	~18.6 @ 300^0 K	1 x 10^{-6} (273^0 K)	45.2	20.2 x 10^{-6}
Number of Isotopes = 25		Isotopic Mass Range 206 - 230		

Naturally Occurring Isotopes

Nuclide	Atomic Mass	Half-Life	Decay Mode and Energy (MeV)
^{223}Ra	223.018501	11.43 d	α 5.72(54%); 5.61(26%); 5.54(9%); 5.50(1%); 5.43(2%) / γ 0.154; 0.122; 0.270; 0.339; 0.031; 0.445
^{224}Ra	224.020186	3.67 d	α 5.69(95%); 5.45(5.5%) / γ 0.241
^{226}Ra	226.025402	1599 y	α 4.78(94.5%); 4.59(5.5%) / γ 0.186
^{228}Ra	228.031064	5.77 y	β 0.040(70%); 0.024(30%) / low E γ

Affinity series for ion exchange among alkaline earths: $Ra^{+2} > Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2} > Be^{+2}$

Distribution Coefficients (D) and Rational Activity Coefficents (ζ) for Trace Ra Co-Precipitation

	$CaSO_4$	$SrSO_4$	$PbSO_4$	$BaSO_4$
D (25^0 C)	~800	280	11	1.8
ζ (25^0 C)	~29.8	215	26.8	1.11

Schematic Reactions Controlling Environmental Behavior of Radium

Adsorption:	$Ra^{+2} + Ba^{+2} + Ca$-(clay/organics/Oxides) = Ca^{+2} + Ra-(clay/organics/Oxides)-Ba
Co-precipitation	$xCa^{+2} + (1-x)Ra^{+2} + MeCO_3 = Ca_xRa_{(1-x)}CO_3 + Me^{+2}$
Surface Reaction	$Ra^{+2} + SO_4^{-2} = RaSO_4$
Soluble Species	$Ra^{+2} + 2Cl^- = RaCl_2$, etc.....

Solubility Product for $RaSO_4$: log Ksp = -10.37
Stability Constants for Inorganic Complexes (Log K_1): SO_4^{-2} = 2.43 ; CO_3^{-2} = 2.48
Stability Constants for Organic Ligands (Log K_1)

Oxalate	Tartarate	Citrate	EDTA	DPTA
1.2	1.24	2.36	7.07	8.5

Sources: Emsley (1991), Molinari and Snodgrass (1990), Langmuir and Riese (1985), Dyck and Jonasson (1986); Sillen and Martell (1964); Kumok (1978); Nathwani (1978); Shoesmith (1984); Pass (1973); Brown, Dairiki, and Doebler (1978)

Table II. ^{226}Ra Activities in Common Igneous and Sedimentary Rocks

		^{226}Ra pCi/g
Igneous Rocks		
	Acid volcanics	1 - 5.11
	Intermediate volcanics	0.5
	Basic volcanics	.01 - 1.3
	Acid plutonics	.001 - 5.00
	Intermediate plutonics	2.6
	Basic plutonics	0.3 - 1.3
	Ultrabasic plutonics	0.1
Sedimentary Rocks		
	Normal Shales	0.4 - 60.0
	Bitumenous Shales	17.0 - 28.1
	Phosphatic Rocks	4.0 - 40.0
	Carbonate Rocks	0.15 - 0.80
	Sandstones	0.2 - 1.5
	Coal	0.89

Data compiled by Jaworowski (1990a; 1990b)

Table III. Reservoirs and Fluxes in the Global Budget of ^{226}Ra

^{226}Ra Ci a^{-1}	Incoming Flow	Reservoir, Reservoir Mass, & Nuclide Inventory		Outgoing Flow	^{226}Ra Ci a^{-1}
?	Sediments	**Crust**		Sediments	?
?	Groundwater	Total Mass (g)	2.38E+25	Surface Water	?
		U (Ci)	1.65E+13	Groundwater	?
		^{226}Ra (Ci)	1.65E+13	Soil	?
		Th (Ci)	1.81E+13		
		^{228}Ra (Ci)	1.81E+13		
?	Crust	**Soil**		Crust	?
?	Groundwater	Total Mass (g)	2.24E+20	Groundwater	?
1.7E+03	Atmosphere	U (Ci)	8.11E+07	Atmosphere (3.5%)	6.5E+03
5.4E+02	Biota	^{226}Ra (Ci)	1.89E+08	Biota	5.4E+02
4.8E+02	O&G sludge&scale	Th (Ci)	1.35E+08	Surface Water	?
1.1E+03	Phosphate Fertilizer	^{228}Ra (Ci)	1.62E+08		
?	Sediments	**Oceans**		Sediments	?
4.6E+03	Atmosphere	Total Mass (g)	1.37E+24	Atmosphere	1.1E+02
2.7E+02	Biota	U (Ci)	1.62E+09	Biota	2.7E+02
5.4E+03	^{238}U *in situ*	^{226}Ra (Ci)	1.35E+08		
6.2E+03	Surface Water	Th (Ci)	1.35E+05		
5.4E+02	O&G produced water	^{228}Ra (Ci)	1.35E+05		
?	Crust	**Groundwater**		Crust	?
?	Soil	Total Mass (g)	4.00E+21	Soil	?
?	Surface Water	U (Ci)	5.41E+06	Surface Water	?
?	Glaciers	^{226}Ra (Ci)	5.41E+06		
		Th (Ci)	-		
		^{228}Ra (Ci)	-		
?	Crust	**Surface Water**		Crust	?
?	Groundwater	Total Mass (g)	1.56E+20	Groundwater	?
2.7E+01	Biota	U (Ci)	1.35E+05	Oceans	6.2E+03
		^{226}Ra (Ci)	2.43E+04	Biota	5.4E+01
1.7E+02	Uranium Milling	Th (Ci)	2.70E+04		
1.6E+02	Coal Mines	^{228}Ra (Ci)	-		
1.9E+02	Atmosphere	**Glaciers**		Groundwater	?
?	Crust	Total Mass (g)	2.40E+22		
		U (Ci)	2.43E+04		
		^{226}Ra (Ci)	5.41E+04		
		Th (Ci)	-		
		^{228}Ra (Ci)	-		
1.1E-02	Extraterrestrial Matter	**Atmosphere**			
1.1E+02	Oceans (aerosols)	Total Mass (g)	5.13E+21	Oceans	4.6E+3
6.5E+03	Soil	U (Ci)	2.70E+02	Soil	1.7E+03
5.41E+01	Coal Burning	^{226}Ra (Ci)	5.41E+02	Glaciers	1.9E+02
1.62E+00	Nuclear materials	Th (Ci)	-	Biota	5.4E-01
2.43E+02	Anthropogenic Particulates	^{228}Ra (Ci)	-		
5.4E-01	Atmosphere	Biota			
2.7E+02	Oceans	Total Mass (g)	2.43E+18	Oceans	2.7E+02
5.4E+01	Surface Water	U (Ci)	8.13E+02	Surface Water	2.7E+01
5.4E+02	Soil	^{226}Ra (Ci)	1.11E+03	Soil	5.4E+02
		Th (Ci)	?	Sediments	2.7E+03
		^{228}Ra (Ci)	?		

Note: Anthropogenic particulates -- underlined text indicates human influenced flux; All data except that for O&G wastes adapted from Jaworowski (1990a; 1990b); O&G waste data based on API (1993); Meyer (1993); EPA/SCA (1991); Banfield (1990); Herczeg, et al. (1988); Kraemer and Reid (1984); Gutsalo (1964).

Table IV. Chemical Characteristics and Behavior of Radon

Radon **Rn**

Atomic Number 86
Relative Atomic Mass (C=12.00000) 222
Discovered 1900 by Dorn @ Halle

Crustal Abundance = trace

Radii x 10^{-12} m — Atomic = na — Hydrated = na

Electronegatvity — Pauling = na — Allred = na — Absolute 5.1 ev

Standard Reduction Potentials (not available)

Electronic Ground State Configuraton $[Xe]4f^{14}5d^{10}6s^{2}6p^{6}$

Oxidation States
Rn^{II} Rn^{+2}, RnF_2

Melting Point ^{0}K	Boiling Point ^{0}K	ΔH_{fusion} kJ mol^{-1}	$\Delta H_{vaporization}$ kJ mol^{-1}
202	211.4	~2.7	18.1

Thermodynamic Properties 298.15^{0}K, 0.1 MPa

State	$\Delta_f H^\theta$ kJ mol^{-1}	$\Delta_f G^\theta$ kJ mol^{-1}	S^θ J K^{-1} mol^{-1}	C_p J K^{-1} mol^{-1}
Gas	0	0	176.21	20.786
Liquid	na	na	na	na
Solid	na	na	na	na

Phase	Density kg m^{-3}	Thermal Conductivity W m^{-1} K^{-1}	Critical T&P ^{0}K / atm	Molar Volume cm^3
Gas	9.73@ 273^{0}K	~3.46x10^{-3} @ 300^0 K (gas)	378^0 / 62	50.5@211^{0}K (gas)
Liquid	4400@ 211^{0}K	na	-	-

Number of Isotopes = 28 — Isotopic Mass Range 199 - 226

Naturally Occurring Isotopes

Nuclide	Atomic Mass	Half-Life	Decay Mode and Energy (MeV)
^{219}Rn (actinion)	219.009479	3.96 s	α 6.8189(81%) 6.5527(11.5%) 6.4246(7.5%) / γ 0.271
^{220}Rn (thoron)	220.011368	55.6 s	α 6.288 (99.9%) / γ 0.550
^{222}Rn	222.017570	3.82 d	α 5.490 (99.9%) / γ 0.510

Diffusion coefficient in air = 0.1 cm^2 sec^{-1}; Viscosity @ 1 atm & 20^{0}C = 229 micropoise

Solubility in water @ 1 atm partial pressure & 20^{0}C = 230 cm^3 kg^{-1}

Solubility in Various Liquids @ 1 atm partial pressure & 18^{0}C (cm^3 kg^{-1})

glycerine	ethanol	liq. paraffin	toluene	carbon disulfide
0.21	7.4	9.2	13.2	23.1

olive oil
29.0

Rn is adsorbed by activated carbon, silica gel and similar materials due to its large size; movement of Rn from a source to the environment depends not only on the amount of Ra present in the source but also on the emanation efficiency fo the substratum

Sources: Emsley (1991), Wilkening (1990); Brown, Dairiki, and Doebler (1978)

Figure 1. The perodic table from a geochemical point of view . (modifed from Goldschmidt, 1954)

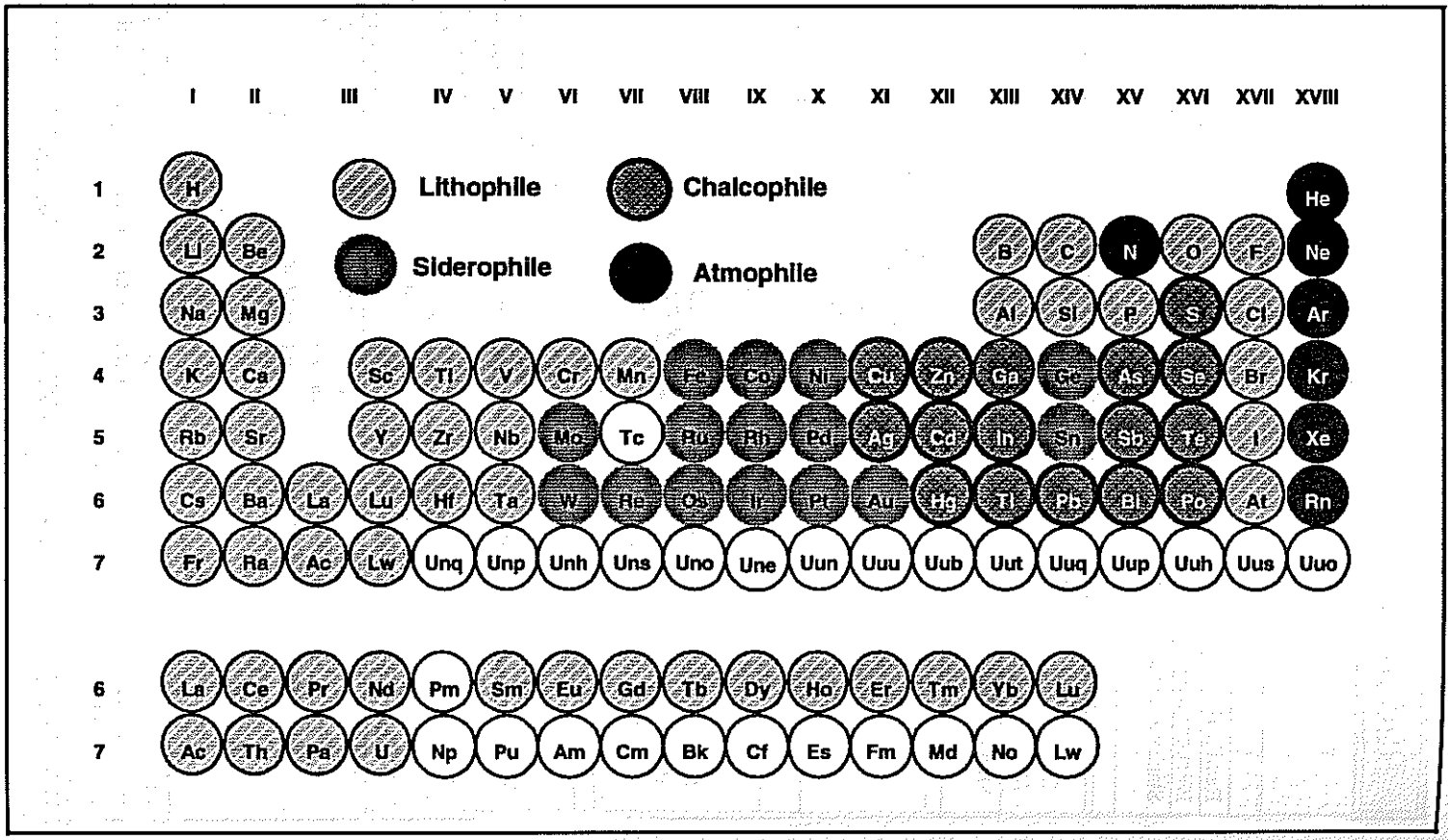


Figure 2. Relationship of Atomic Number to Atomic Volume for the Elements. Please note that this is a plot of atomic volume versus atomic number and not a plot of atomic radius versus atomic number. This was done since there is no way of relating the radii of the nobel gases to those of the other elements. Atomic volume is obtained by dividing the relative atomic mass of an element in grams by its density in grams/cm^3, and is expressed as cm^3, to obtain molar divide this value by 10^6 (data from Lof, 1987 and Emsley, 1991).

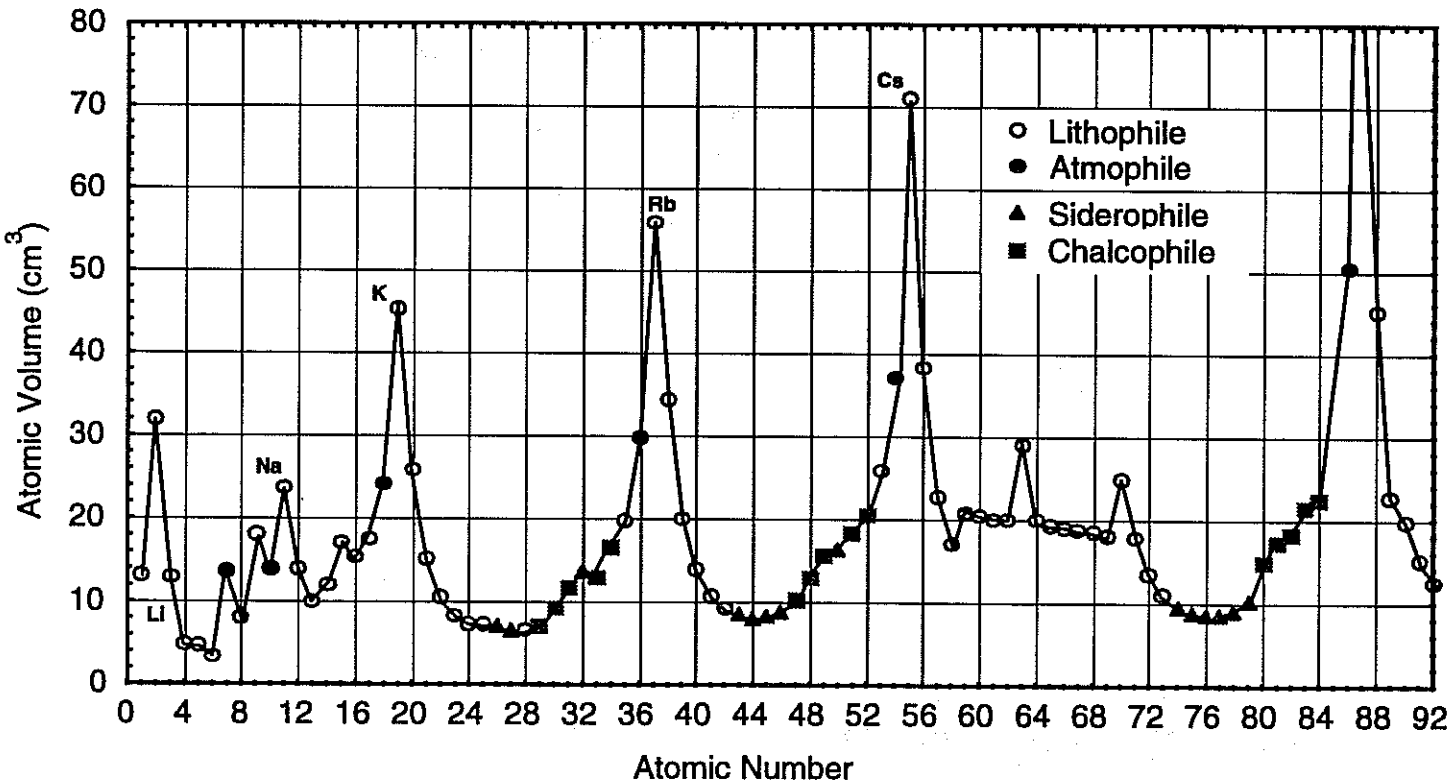


Figure 3. Lithologic and Geochemical Outcomes from Weathering Average Continental Igneous Rock. (Modified from Mason, 1982). The average igneous rock of the continental crust is a granite. Under the influence of chemical weathering, alkali and alkaline earth metals are solubilized and the alkaline earth metals will eventually be precipitated as carbonates. Clays are produced from weathering reactions of feldspars form shales; resistant quartz grains form sandstones. Extreme leaching produces soils.

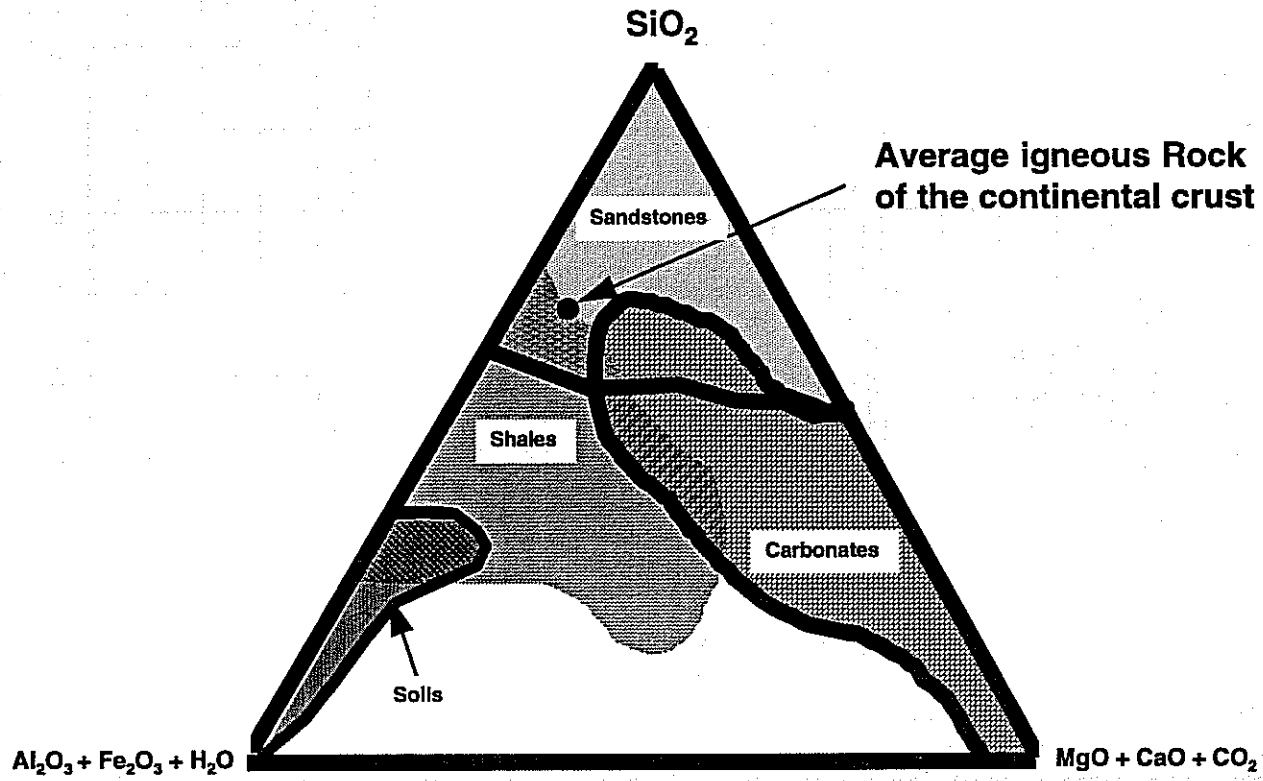


Figure 4. Radioactive decay of the natural actinide elements. (data from Brown, Dairiki, and Doebler, 1978)

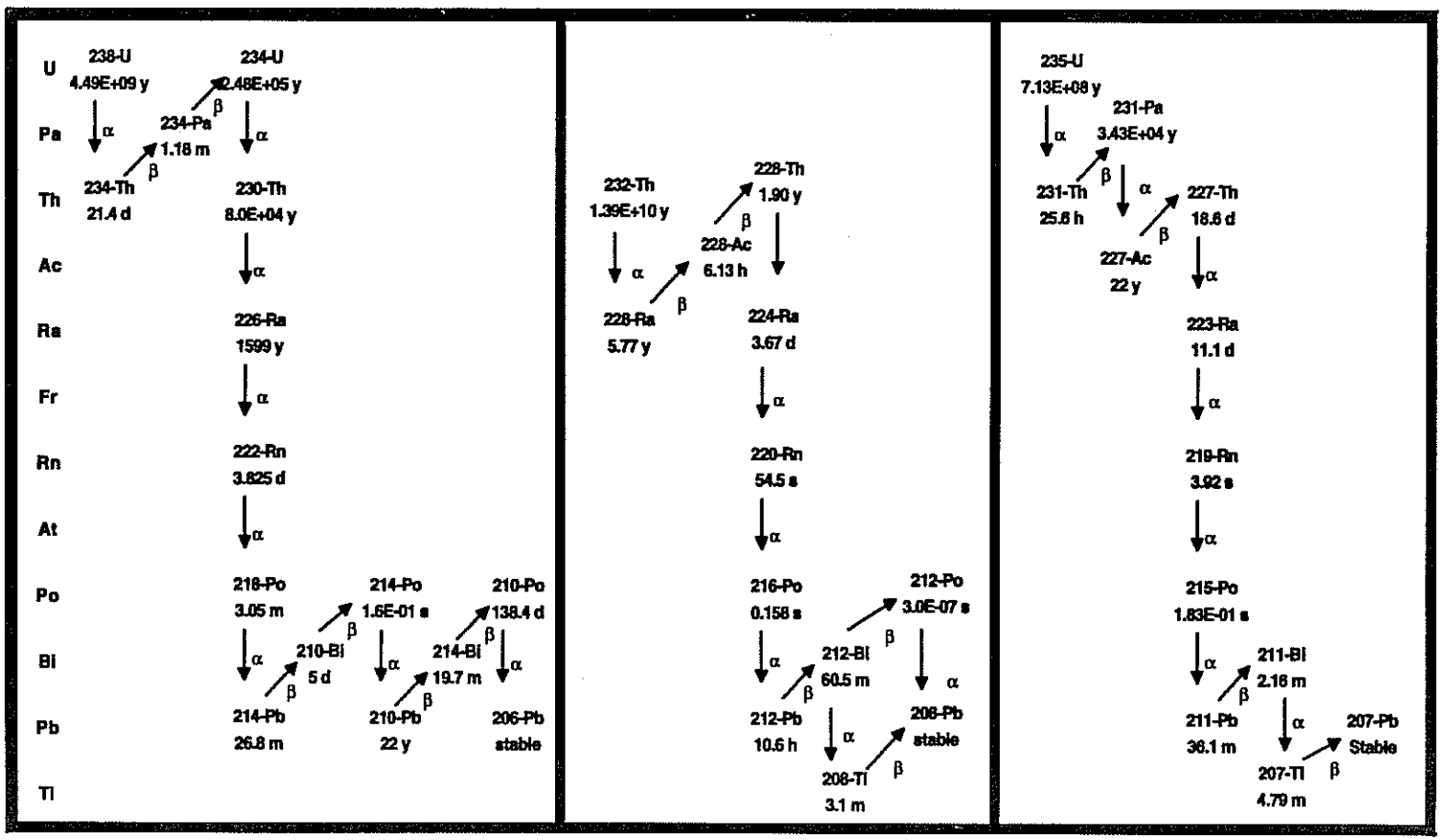


Figure 5. ^{226}Ra and total dissolved solids in some produced waters. At total dissolved solids concentrations above about 5,000 mg/kg, Ra activity appears to vary directly with total dissolved solids content, but the population of observations definitely contains samples which are either substantially more or substantially less radioactive than expected based on the overall trend.

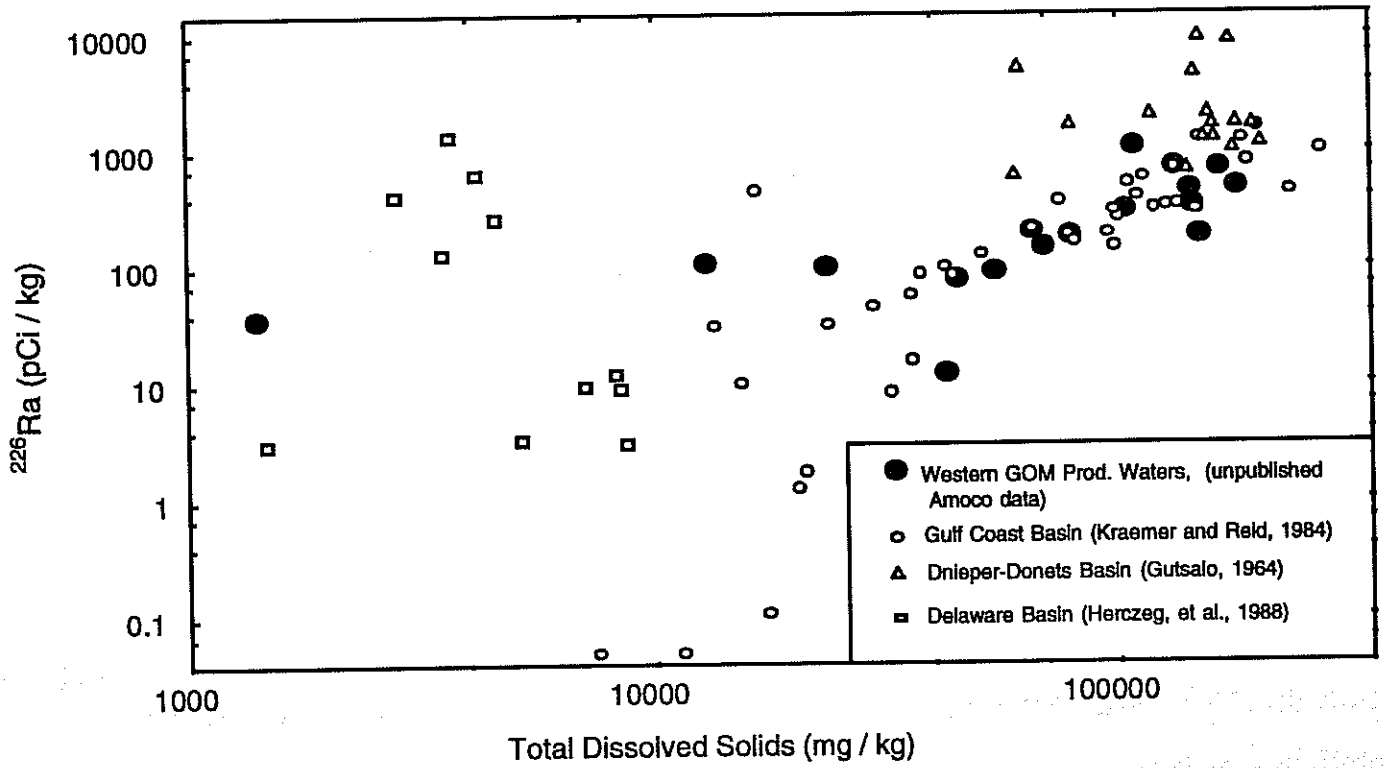


Figure 6. Global cycle of ^{226}Ra showing reservoirs and fluxes (data in Curies or Curies y^{-1}). (modified from Jaworowski, 1990a)

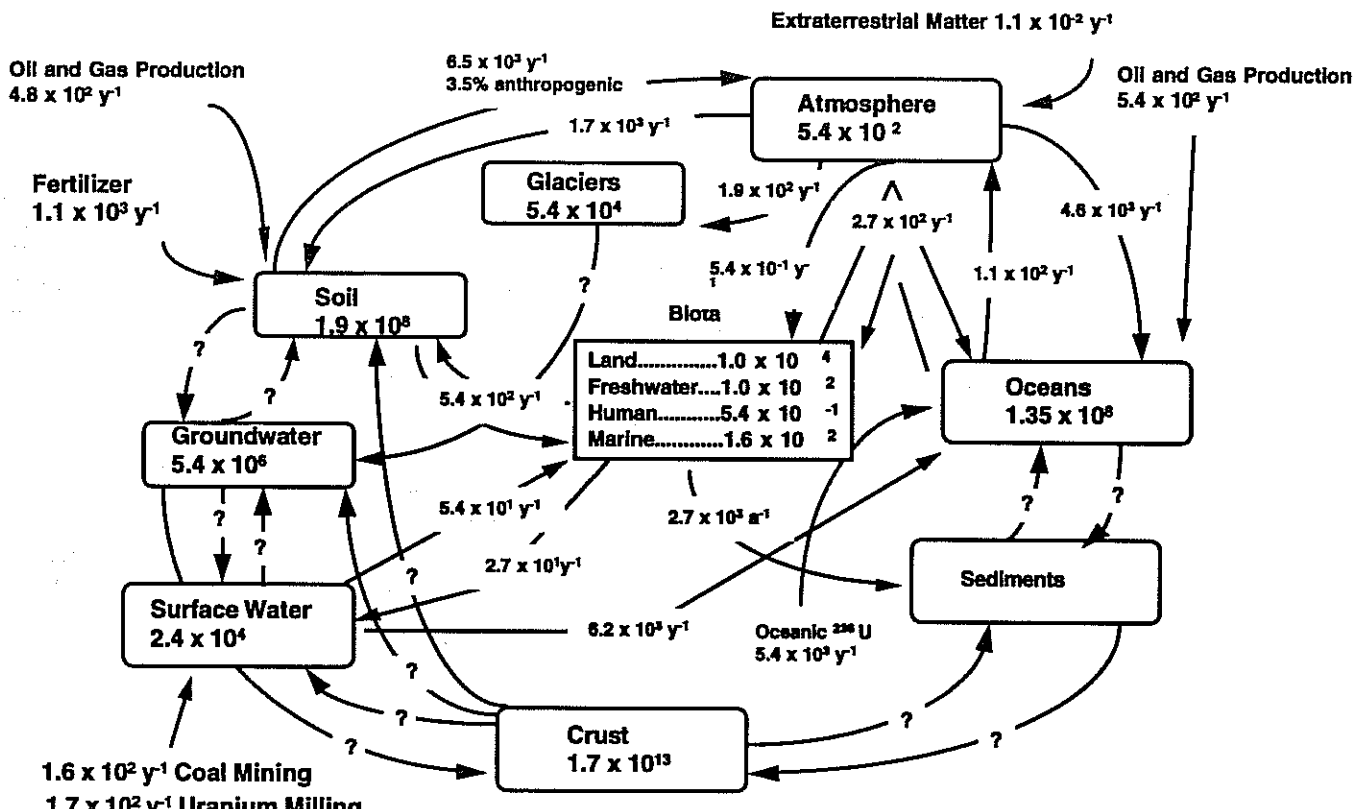


Figure 6. Global cycle of ^{226}Ra showing reservoirs and fluxes (data in Curies or Curies y^{-1}) (modified from Jaworowski, 1990a).

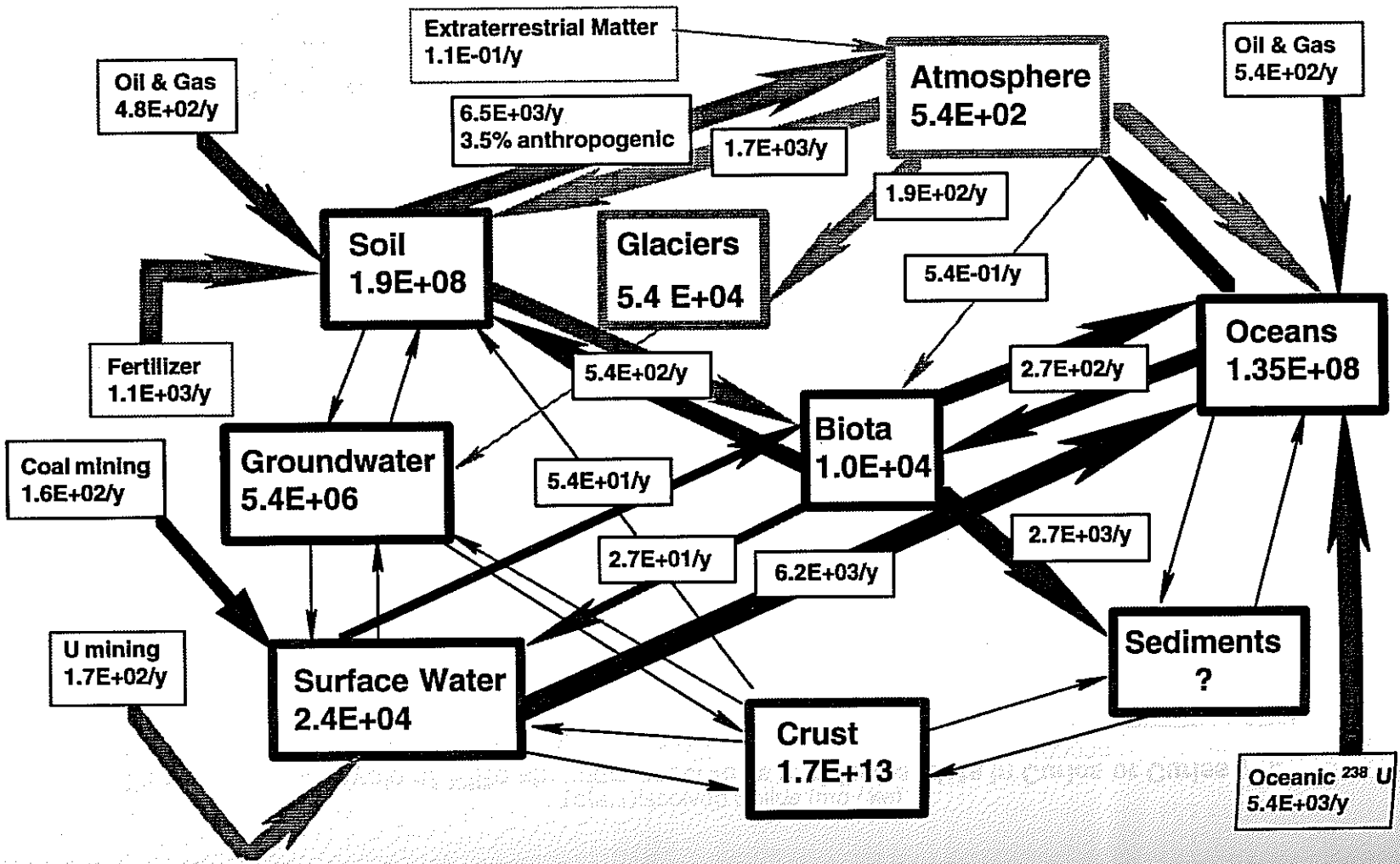


Figure 7. Effect of activated charcoal on ^{222}Rn emanation from a simulated pipe yard soil. The emanation power of dispersed NORM scale particles is much higher than the emanation power of the same NORM scale particles when they are not dispersed. The addition of a minor amount of activated charcoal to this system greatly reduces emanation power of both dispersed and non-dispersed NORM scale particles.

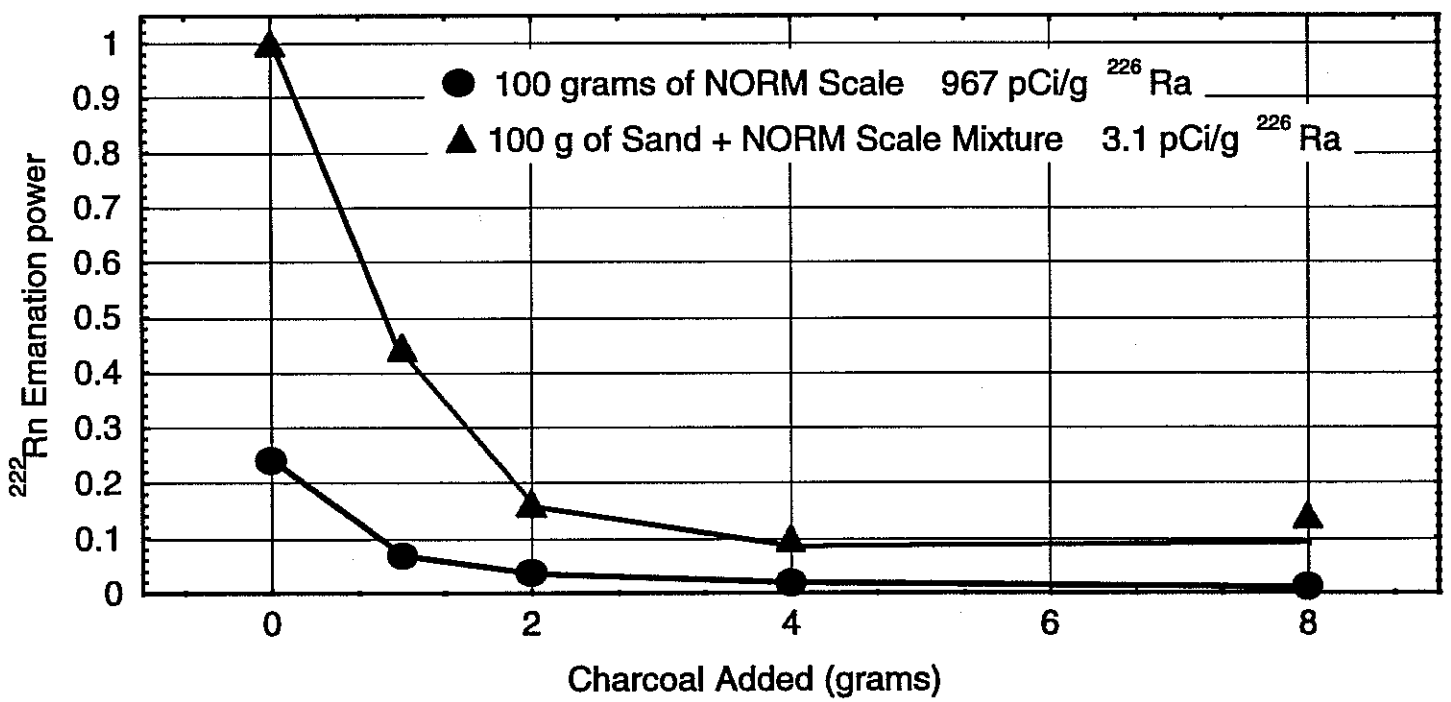


Figure 8. Interaction between Rn decay products, particulates, and environmental surfaces. (modified from Nero (1989). Metallic decay products of radon gas are positive ions and readily attach to surfaces and aerosol particles. Subsequent decay of these metals may detach the decay daughter from the particle or surface through the ejection of an α particle and α recoil of the resulting decay daughter. Aerosols bearing radioactive decay daughters of radon are readily dispersed by advective transport.

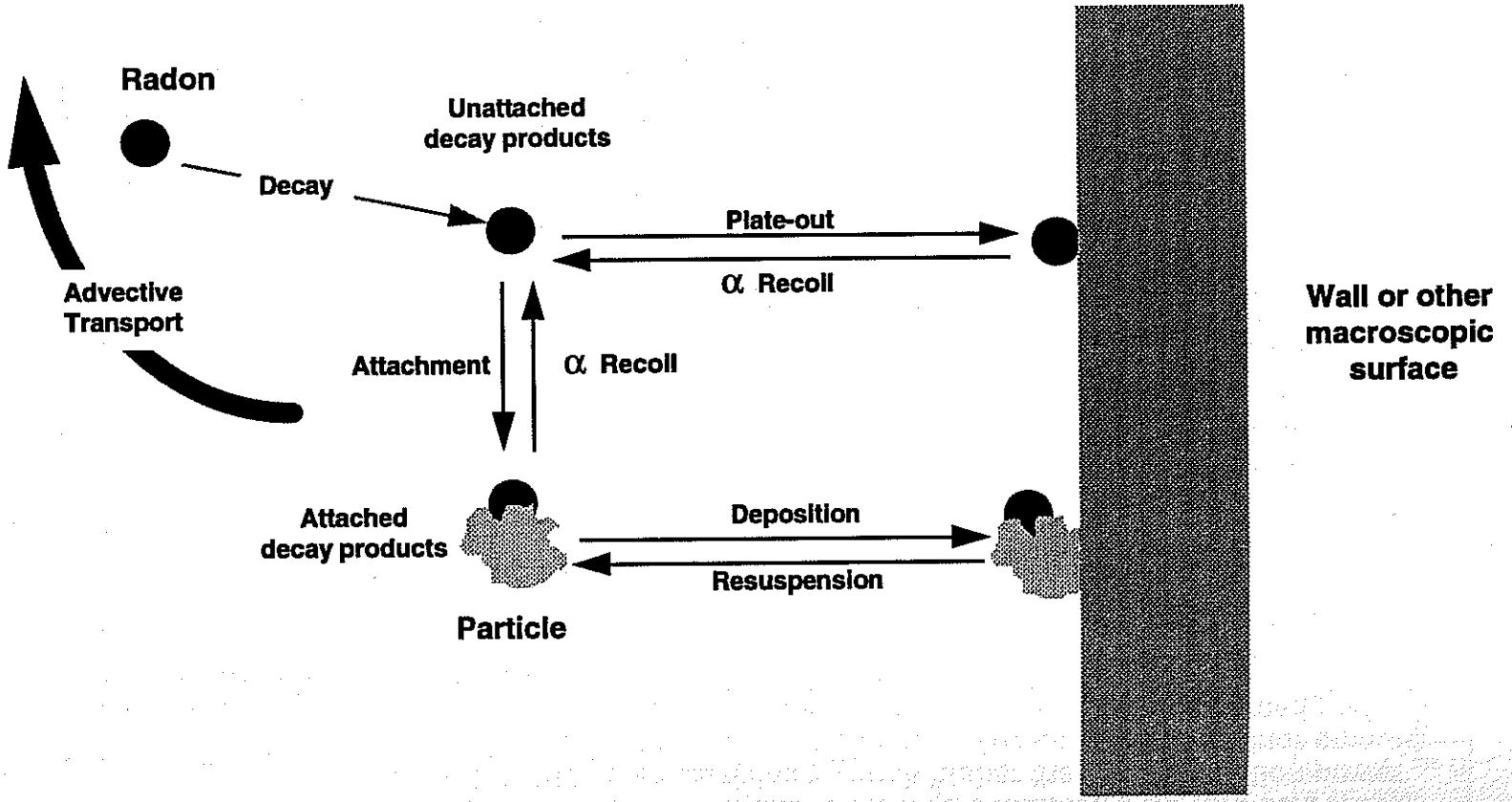
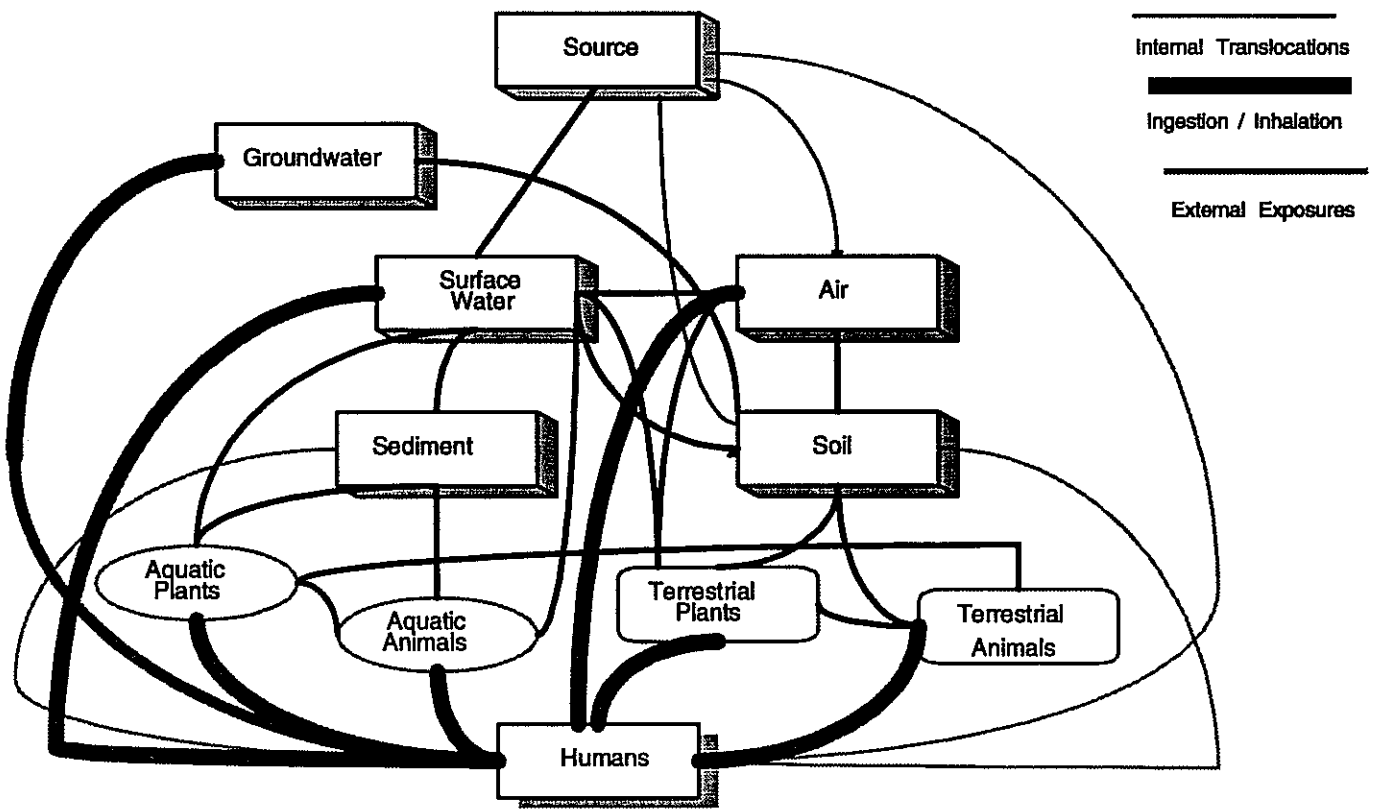


Figure 9. Pathways for the transport of contaminants from a source to humans. (modified from Halbert, et al. 1990)



On-Site and Off-Site Exposure From Naturally Occurring Radioactive Material (NORM) On or In Soil

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Concerns have been raised about the potential for and magnitude of exposure to workers and the general public from NORM deposited on or in soil of unremediated sites. On-site exposure can potentially occur from direct gamma and the inhalation of radioactive particles and gas. Off-site exposure can potentially occur only from the inhalation of radioactive particles and gas. A range of exposure scenarios will be presented with dose estimates. Based on conservative assumptions the potential for exposure to NORM is minimal.

INTRODUCTION

As a result of crude petroleum production, certain land areas may have become contaminated with naturally occurring radioactive material (NORM). Concerns have been raised about the potential for this radioactive material to be taken into the bodies of any persons who frequent such land areas or live near such sites and are thereby exposed to this radiation. The purpose of this report is to estimate the magnitude of this type exposure. This report is not intended to be an estimate of the dose which might result if such land areas were used as home sites.

COMPUTER CODES

Two computer codes, RESRAD *A Manual for Implementing Residual Radioactive Material Guidelines* (ANL/ES-160DOE/CH/8901) [Version 4.6] and MILDOS *A Computer Program for Calculating Environmental Radiation Doses from Uranium Recovery Operations* (NUREG/CR-2011 PNL-3767) were used in this study. RESRAD was developed by Argonne National Laboratory for the U.S. Department of Energy to estimate the radiation dose from radioactive material in soil. Although this code allows for resuspension of particulate and radon emanation, it does not allow for the movement of either particulate or gas off of the contaminated site except by the water pathway. MILDOS was developed by Pacific Northwest Laboratory to estimate off-site radiation doses from uranium refining operations. The principal radioactive waste generated in the uranium refining process is ^{226}Ra. Regardless of the source of the ^{226}Ra, the radiological properties do not change, although other properties such as solubility and radon emanation fractions may be different.

RADIOLOGICAL CHARACTERISTICS OF NORM

Radium-226 is the radioisotope usually associated with petroleum NORM. In some cases, ^{228}Ra may be present. Through the natural decay process, the following radioisotopes will at all times be present at similar concentrations in comparison to ^{226}Ra, if there has been at least a thirty-day lapse since the radium was produced with the crude petroleum: ^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po. Over several decades, three additional radioisotopes will buildup to concentrations similar to those of the isotopes just mentioned. The three radioisotopes are ^{210}Pb, ^{210}Bi, and ^{210}Po. These isotopes, in total, emit alpha, beta and gamma radiation. Since ^{228}Ra has a half-life of 5.2 years, after a few years the exposure potential is minimal.

EXPOSURE PATHWAYS

There are two routes by which internal exposure may occur: [1] inhalation of radioactive particulate and [2] inhalation of radioactive gas. The particulate pathway results from resuspension into the air of radioisotopes in the soil. Through diffusion, ^{222}Rn (a gas) emanates from the soil and becomes airborne. Exposure to ^{220}Rn, a daughter of ^{228}Ra, is of no concern because it has a half-life of 59 seconds.

ESTIMATION OF ^{226}Ra SOIL CONCENTRATION

The usual input for RESRAD is the soil concentration of ^{226}Ra. However, soil concentration measurements are time-consuming and difficult. The common measurement is the microroentgens/hr gamma measurement. By making assumptions regarding the thickness of the contaminated soil and whether or not the contaminated layer is covered with uncontaminated soil, it is possible to calculate backwards to obtain a soil concentration. For example, if it assumed that the contaminated layer is one inch thick and uncovered, then the task becomes only a matter of entering various ^{226}Ra concentrations until the external gamma dose computed by RESRAD equals the observed microroentgens/hr measurement. [NOTE: RESRAD reports in rem units, whereas field measurements are reported in roentgen units. Technically, these are two different units; however, on a practical basis, it can be assumed that these two units are equal without an ensuing error greater than a few percent.] In the presence of any ^{228}Ra, an overestimate of ^{226}Ra soil concentration will result. It was conservatively assumed that there was no ^{228}Ra present.

Considering the NORM to have been on (in) the soil for a period ranging from a few months to several years, it is reasonable to assume that the NORM has most probably mixed to a depth of at least one inch. Additionally, once the contamination exceeds several inches, there is little contribution to gamma measurements from NORM at greater depths. NORM that is in soil at depths greater than six inches contributes little to the gamma dose. [NOTE: Due to the characteristics of ^{222}Rn, NORM at depths greater than six inches can contribute to the dose potential through the ^{222}Rn inhalation pathway.]

If it is assumed that the NORM is not covered by an uncontaminated layer of soil and that the depth is at least one inch but not greater than six inches, a set of curves can then be derived which relate microroentgens/hr readings to ^{226}Ra concentrations. Figure 1 is a set of such curves. By selecting a microroentgens/hr reading, the range of concentrations for NORM deposits (from one to six inches of depth) can then be read off of the curve. For example, if one selects a microroentgen reading of 200

microroentgens/hr, then the estimated soil concentration of ^{226}Ra ranges from 148 pCi/g (six inches deep) to 508 pCi/g (one inch deep). See Figure 1.

ESTIMATION OF INTERNAL DOSE

It is recognized that different types of radiation, namely alpha, beta and gamma, have different levels of biological effects per unit of energy deposited and that different internal organs have various degrees of radiosensitivity. In order to make comparisons, the energy deposited into tissue is weighted so that a given rem dose should result in the same biological effect regardless of whether the energy deposited resulted from alpha, beta or gamma radiation. In other words when dose is given in rem units, it does not matter what type of radiation was the source of the energy deposited. Also to be taken into account are differences in radiosensitivity; the rem doses are weighted so that they represent the same probability of a biological effect as if the dose were to the whole body. When this is done, the resulting dose is designated as the effective dose equivalent (EDE) in rem units. Thus, if one person receives a whole body dose of gamma radiation of 5 rem EDE and another person receives an internal exposure to alpha radiation and when the biological effect weighing and the radiosensitivity weighing are done the EDE is 5 rem, one would expect that each person had the same probability of radiation-induced cancer.

ON-SITE

RESRAD will compute the dose from inhalation of radioactive particulate and radioactive gas. The dose for particulate is from the inhalation of ^{226}Ra and ^{210}Pb. The dose for radioactive gas is from the inhalation of ^{222}Rn. While the materials are in the body, they decay into other radioactive material. Any associated doses from the other materials are taken into consideration when doses are calculated.

Due to the radiological properties of ^{210}Pb, the concentration of ^{210}Pb will buildup over time and reach its maximum some 140 years after the initial production of the ^{226}Ra with the crude petroleum. Due to the long half-life of ^{226}Ra, the dose from ^{226}Ra remains essentially constant throughout this 140-year period. All dose estimates assume that a person is on-site for 2000 hours per year (50 weeks/40 hours per week). Figure 2 depicts the total particle inhalation dose from both ^{226}Ra and ^{210}Pb as a function of time since the initial production of the ^{226}Ra. The initial concentration of ^{226}Ra was assumed to be 500 pCi/g of soil. Since resuspension is a surface phenomenon, the depth of concentration does not affect particulate inhalation dose. Estimates of resuspension range from 2×10^{-4} to 6×10^{-4} (*Data Collection*

Handbook to Support Modeling the Impact of Radioactive Material in Soil, ANL/EAIS-8, April 1993). The most conservative value, 6×10^{-4} (that resulting in the largest dose), was assumed for these calculations. Dose rates from ^{222}Rn will remain essentially consistent over reasonable time periods. Figure 3 is a set of curves illustrating the ^{222}Rn dose versus ^{226}Ra concentrations. From these curves, it is apparent that gamma will contribute most to the total EDE.

OFF-SITE

MILDOS will compute the dose from the inhalation of radioactive particulate and radioactive gas that is generated at the site of the contaminated soil and moved off-site by wind movement. Generic wind parameters are used for these calculations. Input radiological parameters are in curies per year. Radium-226 release can be calculated by assuming an erosion fraction (The RESRAD default value is 1 mm per year) and calculating the volume of material released. The radium concentration can be estimated from Figure 1. As stated above, the amount of ^{210}Pb is a function of how long it has been since the ^{226}Ra was produced. Figure 4 depicts the fraction of ^{210}Pb relative to the ^{226}Ra concentration. Figure 5 depicts the amount of ^{222}Rn that is released over each meter of contaminated soil each second. To get the amount of ^{222}Rn released, just multiply the contaminated area in meters times the number of seconds in a year.

Table 1 presents the dose estimates for various distances downwind from the site of the contaminated soil. The ^{226}Ra and ^{210}Pb releases per year were assumed to be 10 millicuries for each. It was assumed that 1 Ci of ^{222}Rn was released per year. There is a linear relationship between annual release quantities and dose; therefore, if one is interested in doses for different release rates, this can be gotten by calculating the ratio of the release rate of interest to the above rates and then multiply by the applicable table value.

The U.S. Nuclear Regulatory Commission allows for the release of radioactive material into the environment, provided the EDE does not exceed 50 millirem per year. [NOTE: This assumes that the radioactive material is eliminated from the body within one year.]

APPLICATION OF THIS INFORMATION

Suppose that one has a gamma measurement of 600 microroentgens/hr and desires to estimate the total dose a person would receive if that person were to spend 500 hours per year on-site. Based on crude petroleum records, it is estimated that the NORM has been on (in) the ground for fifteen years.

Assumption

- The NORM is uncovered and in a layer of at least one inch, but not more than six inches in thickness

Gamma Dose

- 600 microroentgens/hr x 500 hr/year x 1 millirem/1000 microroentgens
  = **30 millirem/year**

Inhalation Dose

- From Figure 1–Example, concentrations of ^{226}Ra range from
  445 pCi/g (6 inches deep) to **1524 pCi/g** (1 inch deep)
- From Figure 2–Example, the dose for 500 pCi/g ^{226}Ra is
  8.3 millirem/year
- Since there is a linear relationship between dose and concentration, one can ratio to determine dose range for any concentration

Particulate

- 8.3 millirem/year x 445 pCi/g/500 pCi/g
  = **7.4 millirem/year** (6 inches deep)
- 8.3 millirem/year x 1524 pCi/g/500 pCi/g
  = **25.3 millirem/year** (1 inch deep)

Gas

- From Figure 3–Example, the ^{222}Rn dose ranges from
  1.7 millirem/year (1 inch deep) to **3.2 millirem/year** (6 inches deep)
- Thus total EDE ranges are as follows:
  - 30 millirem/year + 25.3 millirem/year + 1.7 millirem/year
    = **57.0 millirem/year** (1 inch deep)
  - 30 millirem/year + 7.4 millirem/year + 3.2 millirem/year
    = **40.6 millirem/year** (6 inches deep)

If in fact the contaminated soil is not covered by uncontaminated soil and its depth is between one and six inches, then the total dose ranges from 40.6 to 57.0 millirem EDE.

External gamma contributes from 53 percent to 74 percent of the dose. Because of the conservative assumptions made in regard to the ^{226}Ra soil concentration and the resuspension factor, the fraction of the total EDE resulting from gamma, in a practical situation, is most likely higher.

Suppose one wants to estimate the dose that a family living .3 km downwind from the site described above might receive. The family consists of an infant, a teen, and an adult.

Assumptions

- The NORM is uncovered and in a layer of 36 inches in thickness
- The area of NORM contamination is 50 meters by 50 meters
- Erosion removes 1 mm (.001) thick layer of soil per year

Radium Transported Off Site Per Year

- As previously stated, essentially all of the gamma dose results from the top 6-inch layer; therefore we can use the estimate of ^{226}Ra concentration (445 pCi/g) calculated above for a 6-inch layer
  - .001m x 50m x 50m x 10^6 cm^3/m^3 x 445 pCi/g x 10^{-9} mCi/pCi x 1.6 g/cm^3 = **1.78 mCi/year**

Lead Transported Off Site Per Year

- From Figure 4, the relative activity of ^{210}Pb to ^{226}Ra after 15 years is .38
  - .38 x 1.78 mCi ^{226}Ra = **.68 mCi/year** ^{210}Pb

Radon Transported Off Site Per Year

- From Figure 5, for a ^{226}Ra concentration of 445 pCi/g the radon emanation per m^2 - sec is 56 pCi
  - 56 pCi/m^2 - sec x 50 m x 50 m x 3.15 x 10^7 sec/year x 10^{-12} Ci/pCi = **4.41 Ci/year**

Off-Site Dose

- ^{226}Ra

  From Table 1, infant dose .3 km downwind is 5.77 millirem/year/10 mCi
  - 1.78 Ci/year ÷ 10 mCi x 5.77 millirem/year/10 mCi = **1.02 millirem**

- ^{210}Pb

  From Table 1, infant dose .3 km downwind is 10.60 millirem/year/10 mCi
  - .68 Ci/year ÷ 10 mCi x 10.60 millirem/year/10 mCi = **0.72 millirem**

- ^{222}Rn

  From Table 1, infant dose .3 km downwind is 0.12 millirem/year/Ci
  - 4.41 Ci/year ÷ 1 Ci x 0.12 millirem/year/Ci = **0.53 millirem**

Total Dose

- 1.02 millirem + 0.72 millirem + .95 millirem = **2.69 millirem/year**

Similar dose for estimates for the teen and adult are 0.88 and 0.78 millirem/year, respectively.

NOTE OF CAUTION

Although it is believed that the above data are accurate enough for planning purposes and for developing a feel for doses site specific data will yield more accurate estimates.

SUMMARY

Procedures and data are presented that will allow for the estimate of on-site and off-site dose for a range of ^{226}Ra concentrations.

The on-site and off-site does estimates for typical conditions are below the recommended limits.

Table 1

Off-Site Dose Estimates

Distance Downwind	Subject	Millirem per Year			
		^{226}Ra	^{210}Pb	^{222}Rn	Total
0.1 km	Infant	27.75	51.10	0.48	79.33
	Child	8.40	14.60	0.48	23.48
	Teen	5.61	9.88	0.48	15.97
	Adult	4.10	6.98	0.48	11.56
0.2 km	Infant	11.51	21.20	0.22	32.98
	Child	3.49	6.04	0.22	9.75
	Teen	2.33	4.10	0.22	6.65
	Adult	1.70	2.90	0.22	4.82
0.3 km	Infant	5.77	10.60	0.12	16.49
	Child	1.70	3.02	0.12	4.89
	Teen	1.16	2.05	0.12	3.33
	Adult	0.85	1.45	0.12	2.42
0.4 km	Infant	3.47	6.39	0.07	9.86
	Child	1.05	1.82	0.07	2.94
	Teen	0.70	1.24	0.07	2.01
	Adult	0.51	0.87	0.07	1.45

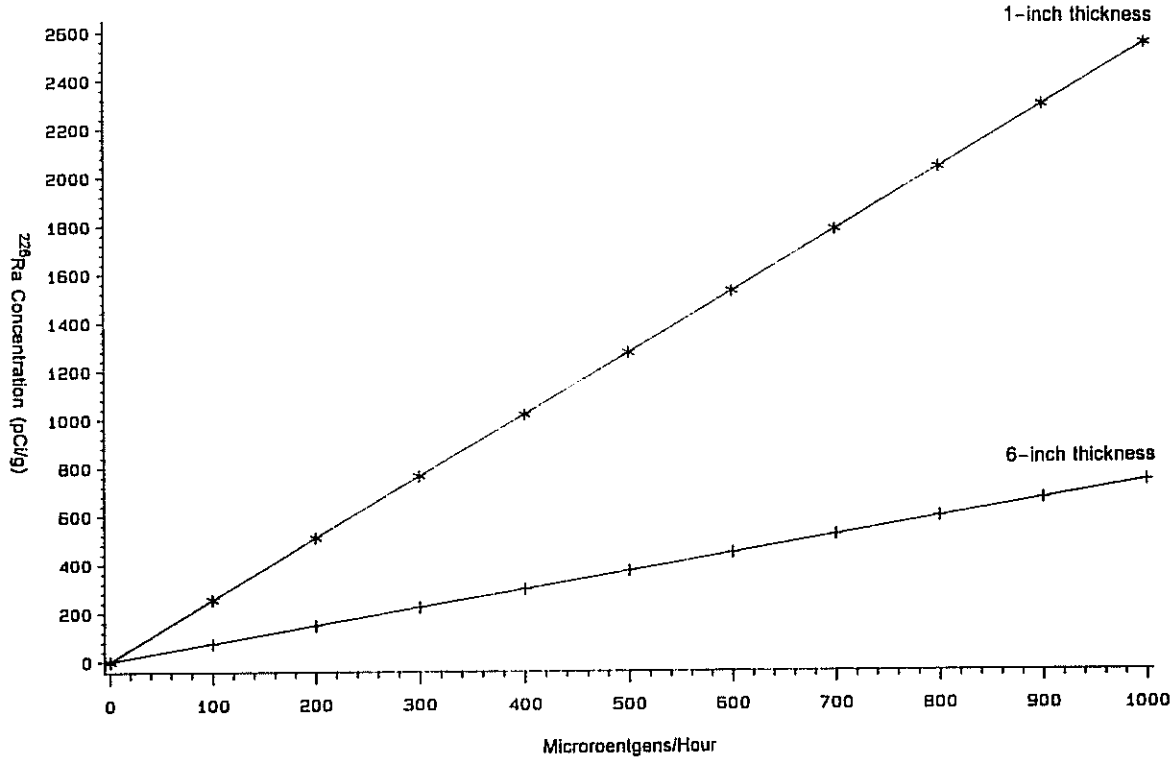

Figure 1. Microroentgens/Hour versus ^{226}Ra Concentration for 1- and 6-inch Contamination Depths

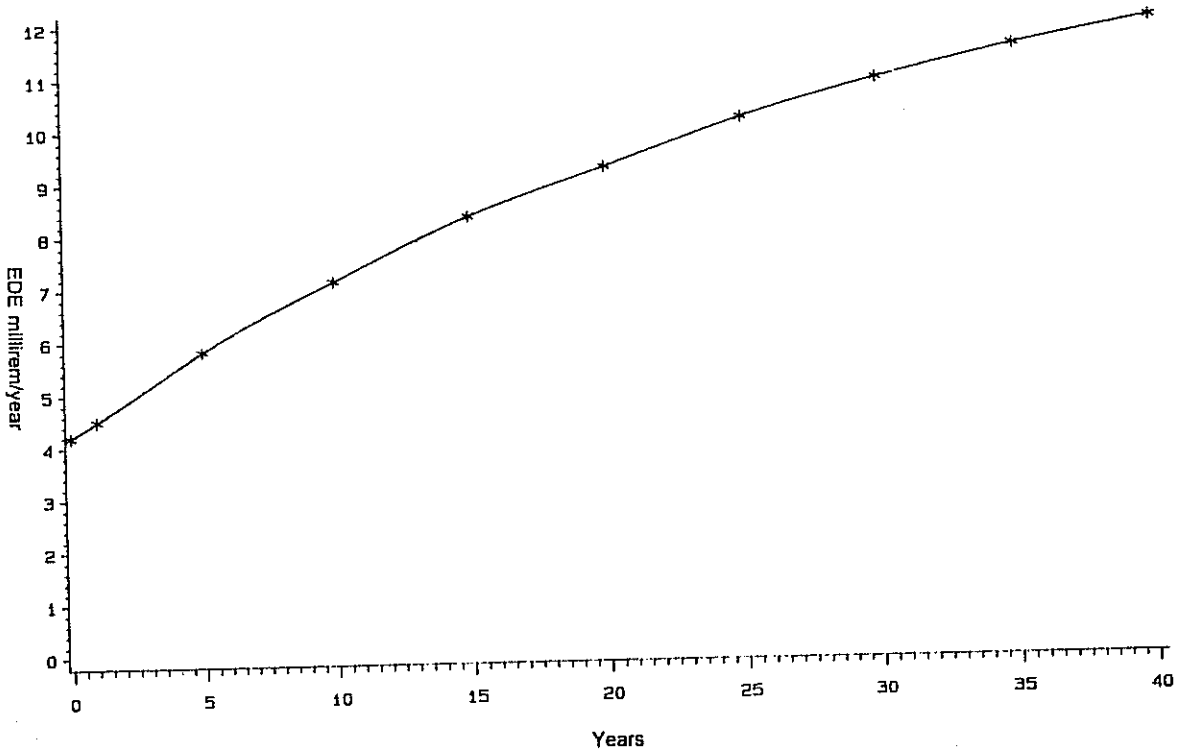

Figure 2. Particle Inhalation Dose versus Time Since ^{226}Ra Produced (500 pCi/g)

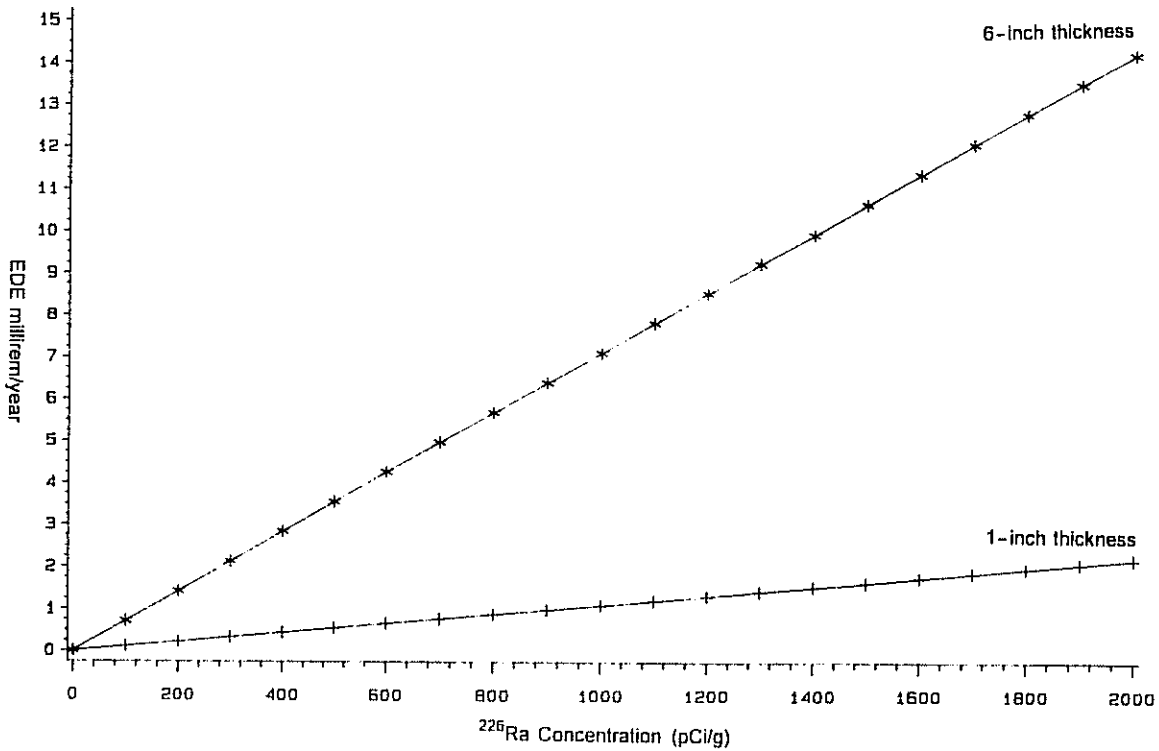

Figure 3. Radon Inhalation Dose versus ^{226}Ra Concentration for 1- and 6-inch Contamination Depths

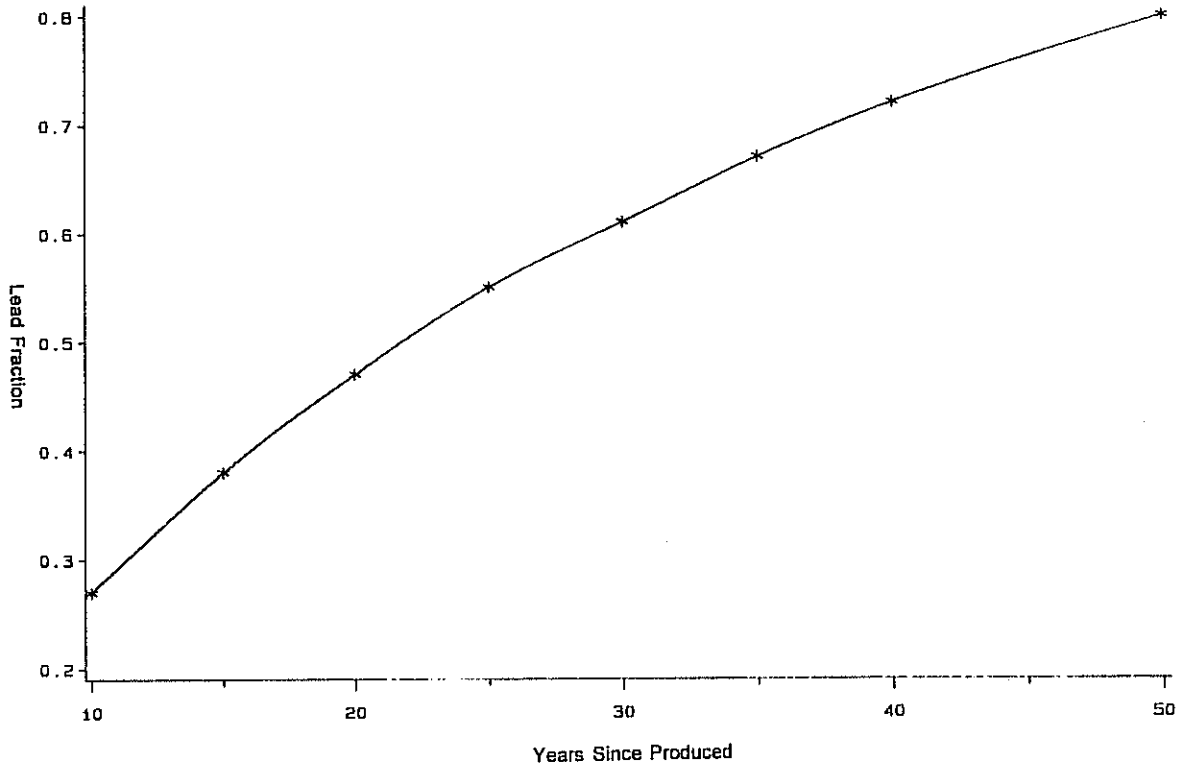

Figure 4. ^{210}Pb versus ^{226}Ra Over Lapsed Time

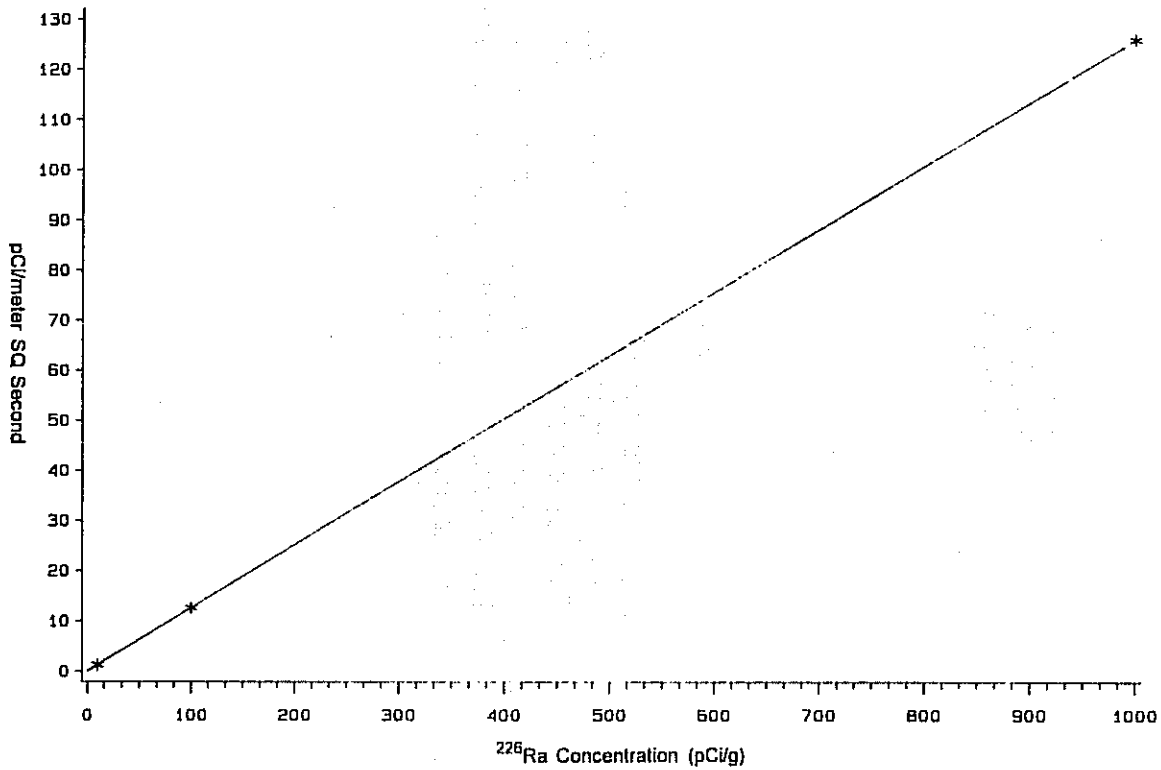

Figure 5. Radon Flux versus ^{226}Ra Concentration

Bounding Risk Associated With NORM in Oil and Gas Operations

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Abstract

When NORM is present at an oil or gas operation, the risk associated with its presence needs to be assessed using a risk assessment approach. Unfortunately, the assumptions that go into a standard risk assessment are limiting factors in developing a rigorous, objective mathematical treatment of the problem. This paper discusses the problem from a societal, regulatory, risk management, and risk assessment approach with emphasis on defining and statistically bounding the upper limit so as not to rely on a 'worst case' approach that overstates the risk.

INTRODUCTION

We live in a society whose technological advances have provided many benefits including a very high standard of living. With the advances in technology and improved measurement methods that it has brought, there is heighten awareness today regarding health risks. Radiation exposure is one such area that has come under increasing review for possible regulatory action. Although the medical industry successfully uses this technology for beneficial use in its fight against cancer and in the diagnosis of diseases, concerns persist with regard to long tern exposure to radiation, especially low levels. Although, it is acceptable to receive massive doses of high energy radiation for the treatment of cancer. Exposure to low levels is view with alarm. This alarm arises from a concern that low level radiation exposure will induce the same disease that high levels of radiation are used to treat.

Radiation exposure sources include not only man made or technologically enhanced sources (common in the medical industry) but also natural radiation sources. The naturally occurring radioactive material or NORM for short, has part of its origin from radioactive nuclei that are well distributed throughout the earth's outer crust[1]. In addition to this naturally occurring radionuclides, the earth is constantly exposed to cosmic radiation from the sun and other external sources which create radioactive nuclei such as carbon 14[1].

Natural radiation exists everywhere on the earth. All people have a small amounts of radioactive material in their body[1]. The exposure to low levels of radiation is constant and relentless. The concern is over the amount of such exposure to radiation. The assumption is that the greater the amount of exposure or dose, then the more likely the person exposed is to develop cell mutations and cancer. The problem arises from trying to determine limits of exposure and how to quantitatively evaluate the health effects of very low levels of radiation exposure. One tool to do this is risk assessment which uses models to predict adverse health effects.

Risk is an often used word and may be defined as the probability of something occurring or not occurring. In statistical terms, the occurrence is referred to as an event. In some cases the event is beneficial, such as a person winning a lottery. In other cases, the event is adverse or unwanted, such as a material failure. Understanding risk allows us to estimate the probability of an outcome, plan for an adverse happening and manage its consequences. While adequate data exists to predict the risk of events such as fatalities per passenger The problem is that health risk with cancer endpoints involves long term

mile for travel via airlines, cars, and trains, similar data does not exist for the vast majority health related problems. This is especially true for determining how exposure to environmental hazards leads to cancer. About 20-25 % of the populace will get some form of cancer during their lifetime[2]. However, the role of environmental hazards is not fully understood in the cause and effect relationship and models are assumptive at best where data does not exist.

The term risk assessment is generally used to mean the characterization of potential adverse health effects from human exposures (as suggested by the National Academy of Science[2]) with four major steps[3]:

1. Hazard Identification
2. Dose-response Assessment
3. Exposure Assessment
4. Risk Characterization.

The actual management of the risk is usually referred to as risk management. This is the process of evaluating alternative actions and selecting the most beneficial method for avoiding or reducing an unacceptable risk.

Risk assessment and risk management are independent activities and should be kept separate[4]. Risk assessment is a scientific and technical activity. Risk management is a policy and value oriented activity. The independence of the two activities does not mean that there should not be communication between them. To function properly risk management needs the information available from the risk assessment process. Similary, risk assessment costs can be reduced by considering risk management guidelines. This paper will address both of these processes in discussing bounds for NORM in the oil and gas industry.

However, risk considerations address only part of the problem. Legal implications for NORM are dependent upon both state and federal laws and regulations. State regulations vary by state and do little to identify and bound the risk associated with NORM. For example, current regulations, which can be found elsewhere in more detail[5-8],provide exemptions for some sources of NORM because of "beneficial"value and impose limitations on others without the benefit of data to determine or justify the actual risks associated with various different sources and their exposure. Oil and gas industry operations have historically been governed by state regulations for controlling NORM. This is remains true for recently promulgated regulations.

Interestly, there are different legal definitions of NORM by various government agencies. Sometimes the definitions, such as technologically enhanced naturally occurring radioactive material address processes that unintentionally concentrate naturally occurring radioactive nuclei[6]. Thus, naturally occuring radioactive material has been replaced with a process. In these case, the process and its products that are subject to regulation.

NORM regulations impact many different industries and operations such as filtration systems for drinking water, residuals from mineral extraction such as phosphogypsum tailings, and fly ash residues from power plants. For the purposes of this paper, however, NORM will specifically refer to those radioactive materials and operations associated with the oil and gas industry. This type of NORM is most predominant as a scale deposit inside of oil field equipment and the main radionuclide of interest is radium 226 because of its unusually long half life of 1600 years and its solubility in water[11]. There is a substantial amount of literature[10-15] that describes the chemistry in more detail and the occurrence of NORM in oil and gas operations.

The challenge for the oil and gas industry is to manage NORM in operations and satisfy the growing number of state regulations for NORM. This behooves the industry to quantify or bound the problem of health exposure and address the subsequent disposal of contaminated materials. For this task, risk assessment is one way to obtain some understanding and try to arrive at risk management decisions to minimize or eliminate problems for handling and disposing of NORM in the oil patch.

STATEMENT OF THE PROBLEM AND DISCUSSION

Radioactivity is not new to the oil and gas business. It has been known to be associated with natural gas production since 1918, when a Canadian paper[15] was published on this subject and since the 1930's when elevated radium levels were reported from Russian oil fields[16]. What is new, is the regulatory focus on handling and disposal of very low levels of radioactive waste associated with oil and gas operations.

Most current state regulations grant an operator a license to possess, handle and transport NORM at or above the regulatory level for that State by virtue of having regulatory amounts of NORM on a lease site. In some cases, the State may require the registration or licensing of the site for a fee[6]. In other cases, the State may exempt the site so long as

the site and any associated equipment are in operation[8]. These approaches do not relieve the operator of the responsibility of practicing good health physics and complying with all relevant laws for the safe handling of radioactive materials. It is for these reasons that risk assessment is an excellent tool to evaluate such operations.

The termination of operations and abandonment of a NORM contaminated piece of equipment or property in many states involves regulations which have special requirements and limits for remediation and restoration of the physical site and/or disposal of the associated operating equipment. In many cases, the exemption for operating is no longer in effect if the equipment is out of service or if operations are terminated. In the case of terminated operations different regulations or requirements may apply that are dependent upon the state. Generally, it is better to developed an abandonment plan before the production operations are terminated. This provides time to develop disposal options that could include transfer of materials and equipment to other NORM leases or operations, or maintenance and clean-up of the equipment as part of standard operating procedures.

The problem for oil and gas operations can be simply stated: Determine if NORM is present (identification of the hazard), and, if it is present, assess the risk to deal with it (determine the dose-response for the amount of NORM on the site and the exposure pathways for the type of NORM on the property).

A solution to the problem is risk management and can be accomplished through risk assessment which requires establishing the dose-response for type and amount of NORM and determining the exposure pathways. Unfortunately, this requires assumptions, and these assumptions are the limiting factors in developing a rigorous, objective mathematical treatment of the problem. As stated earlier, this is due to a lack of data at the low radiation levels of NORM in oil and gas operations.

Even today, with all of the extensive data on cancer induction by radiation, one is left with the hypothesis, at least with respect to cancer induction and hereditary genetic effects, that the frequency of such effects increases with low-level radiation as a linear, non-threshold function of the dose[17]. Clearly, the quality of life for most people on earth requires the acceptance of some risk from radiation since the elimination of all radiation sources is not possible. One purpose of this paper is to explain the risks of the upper bound of those exposures.

RISK ANALYSIS

Risk analysis may be time consuming and costly to perform. There are different levels of calculations that one can perform dependent upon the detail required[19]. One approach to reducing the cost is to develop limits or bounds for generalized cases and apply those limits or bounds to many problems or conditions. The difficulty with this approach is that it usually creates a very conservative set of values or a very low limit in order to address multiple conditions.

Another problem with determining realistic risk assessment values lies in the uncertainty inherent in the dose-response experiments with animals, typically laboratory mice or rats. Even with cancer prone rats, daily administered doses of chemicals are adjusted just below the toxicity level to generate sufficient cancers for statistical analysis. The use of Monte Carlo simulations can improve the accuracy[19] but according to Rodricks[20], risks of less than 10% (0.1) are very difficult to detect in standard toxicity tests because of a lack of statistical resolving power. As a general note, the risk factors for radionuclides such as radium 226 and 228 are based upon epidemiological data, not animal dose-response data. Therefore, the level of uncertainty in the calculation is much less than expected for a carcinogen whose cancer potency factor (CPF) comes from animal data.

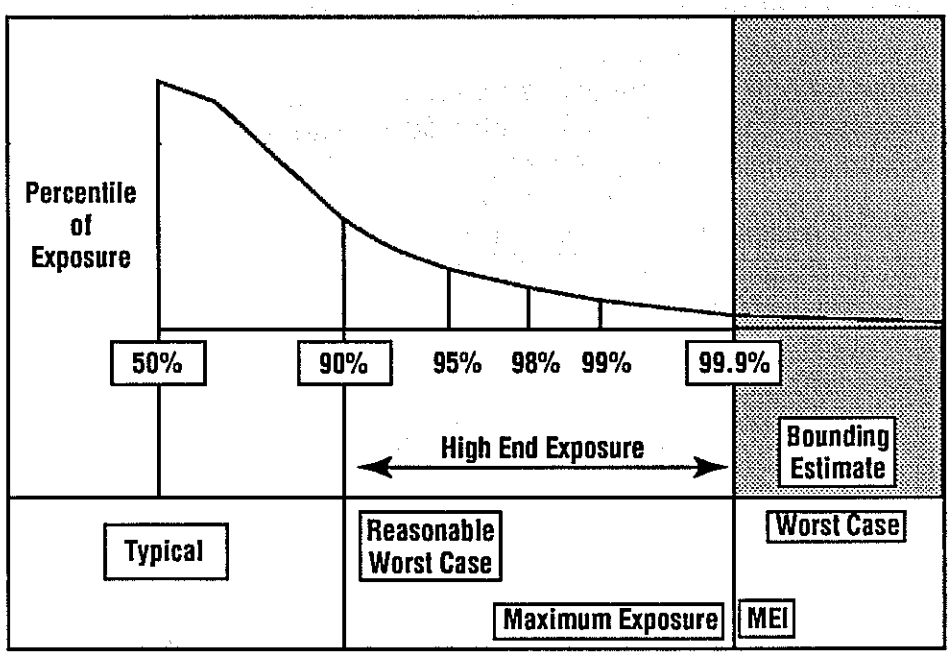

Figure 1: Probability Distribution Of Exposure

The problem is that health risk with cancer endpoints involves long term exposure to low dose levels of carcinogens. The task for the risk assessor becomes how best to extrapolate animal test results or epidemiological data to environmental exposures where risks are in the 1 in 1,000 (0.001) to 1 in 1,000,000 (0.000001) range. The EPA's approach is to use a linear, non-threshold model. With this model all exposure accumulates over a lifetime and leads to cancer. In addition, the EPA wants to protect the so-called maximum exposed individual or the most sensitive individual, so the upper bound of the 95% confidence level is used for the calculation. This translates into a 99.9% or greater upper bound for the probability distribution (See Figure 1) for the most exposed individual (MEI).

For ingested radionuclides, such as radium 226, Norris[9] and co-workers were able to show that the linear model was not applicable for a group of exposed individuals commonly referred to as the dial painters group. Based on their studies, the Norris Retention Equation (1) was developed:

$$R_t = R_o \times 0.54 \times t^{-0.52} \qquad (1)$$

In the above equation, R_t is the amount of radium remaining in the body after some time t; R_o is the dose of radium; and t is the time in days since the dose entered the human body. Figure 2 shows the exponential dependence of the Norris equation with actual normalized retention data from the dial painters group given in Table 1 superimposed on the graph. It is important to note that this is for relatively high ingestion levels of radium exposure and one is faced with a large extrapolation to the low levels of radium associated with NORM.

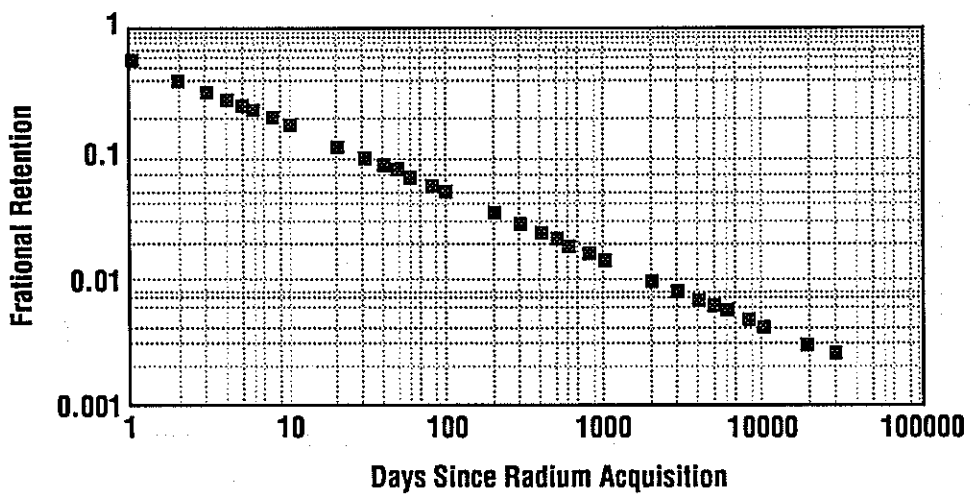

Figure 2: Norris Retention Curve

Time (days)	0	1	10	100	1,000	10,000
Rt/Ro	1.0	0.54	0.16	0.049	0.015	0.0045

Table 1: Normalized retained radium values with time from Norris study of Dial-painters

If a more realistic model, such as the multi-stage fitted model[20], is used, the model results stated as cancer risk in the case of bone sarcomas per person-year rapidly approach zero at low concentrations (see Figure 3). Even with this model, for the 95% limit, as a worst case, one has the interior region of the dashed line in Figure 3. When this confidence range is integrated over the entire domain of the problem, the probability becomes equivalent to a person exposed to an order of magnitude or greater of dose in predicting the long term risk.

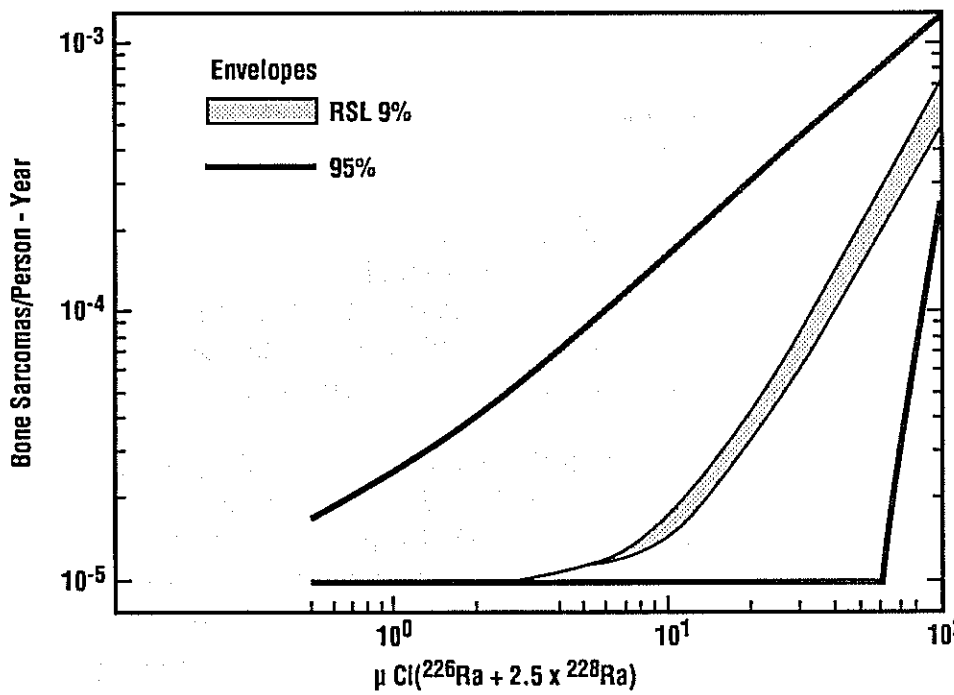

Figure 3: Dose-Response Curves For Radium 226 And Radium 228

Another way to view the differences in these two approaches is to look at the ratio between the slope of the two bounding curves, remembering

that the slopes are the risk coefficients for that dose-response concentration. This becomes the input for the risk calculation. Mathematically, one can express this with Equation (2) as the ratio of the 95% confidence range to the central value:

$$(I_u - I_l) / I \qquad (2)$$

where I_u is the upper limit risk coefficient, I_l is the lower limit risk coefficient, and I is the central value risk coefficient. The lower the value of this ratio, the better the bound on the central value. In Figure 3 this value increases with decreasing intake from 470 at a dose of 0.5 μCi to 4700 at a dose of 0.05 μCi. These high ratios emphasize, in quantitative terms, the ignorance of risk at low exposure levels. The following quote best summarizes the difficulty.

> "These risk data are not unique. Other functions can be determined that meet this 95% probability criterion. The emphasis here is that there is no unique way to specify the uncertainty in risk at low exposures when the shape of the dose response curve is unknown. Regardless of the functions selected at the envelope boundaries, however, the percent uncertainty in the risk cannot be materially reduced." [18]

This problem points out the limitation of statistical differentiation for such low values. This is analogous to one summing up probabilities for each time interval of exposure with a very large upper bound to obtain a large number of questionable accuracy or a high probability of occurrence for a questionable or insignificant portion of the population.

In the face of what appears to be limited applicability, an example is constructive to show the actual values derived from such a calculation. An example is chosen from a paper[19] by the authors for an offshore environment where a platform worker is assumed to catch fish from the platform and eat all the fish he catches. The radium source is assumed to be the produced water discharge from the platform which is diluted in the ocean as it is discharged. The fish bioaccumulate levels of the radium in their bone and tissue as a function of the radium concentration in the water. Radium concentrations in water in pCi/L can be related to risk factors developed for intake of radium in drinking water[1]. The equation that relates these parameter into a risk format is:

$$\text{Risk} = \Sigma\, W_f \times T_W \times CF \times RF_i \times C_i \times (Ra^{226} + Ra^{228}) \qquad (3)$$

where Risk is the lifetime risk (dimensionless), Wf is the concentration of fish consumed in kg/yr, T_w is the workers time on the platform, CF is the bioaccumulation factor (L/kg), RF_i is the lifetime risk factor (1/pCi), Ci is the radium concentration (pCi/L), Ra^{226} is the concentration of radium 226 in the water and Ra^{228} is the concentration of radium 228 in the water.

The risk assessments are calculated using both Monte Carlo simulations with Latin Hypercube Sampling (LHS) and conventional worst case or upper bound limits. The results are summarized in Table 2 and show the superiority of the Monte Carlo methods for estimating the most exposed individual by reducing the risk by one or two orders of magnitude. In the case of the least exposed individual the Monte Carlo methods actually increase the risk by over three orders of magnitude. This narrowing of the limits is a result of the Monte Carlo methods of statistical averaging to improve the estimate for the true or mean value. However, EPA is always concerned with the most exposed individual and both methods in this case give results that are within the safe risk area set by EPA of being less than 10^{-4}.

Total Risk Method	Maximum (95 % CL)	Most Likely (Mean)	Minimum (5 % CL)
Traditional Method for Ra^{226}	1×10^{-5}	3×10^{-8}	2×10^{-13}
Monte Carlo Method for Ra^{226}	1×10^{-7}	2×10^{-8}	1×10^{-9}
Traditional Method for Ra^{228}	9×10^{-6}	3×10^{-8}	6×10^{-13}
Monte Carlo Method for Ra^{228}	1×10^{-7}	2×10^{-8}	1×10^{-9}

Table 2. Comparison of lifetime risk from radium 226 and radium 228 at three different exposure levels using traditional and Monte Carlo calculation techniques.

In a similar way, one can undertake to determine the exposure pathway, the dose-response and exposure for workers in an onshore environment where soil or pipe scale is the principal source material and develop a similar risk assessment. From this data, either by traditional or Monte Carlo analysis techniques, one can evaluate the risk and provide this information to the risk manager to determine suitable action.

From this type of information the risk manager can easily develop any

necessary health and safety plans warranted. In general, none will be warranted due to the low levels for ingestion of radionuclides associated with NORM. Under certain work operations for pipe repair work where systems will be opened and scale deposits exposed, a mask and gloves should be considered as a safety precaution for prevention of inhalation of scale dust particles.

Unfortunately, state regulations vary in dealing with NORM and risk assessment does not relieve an operator from complying with sate NORM regulations. It does provide a basis for satisfying worker safety and liability issues. This later point is significant since state exemptions for ongoing oil and gas operations do not relieve the operator from good health physics practices.

At abandonment, NORM contaminated equipment usually falls into three categories: disposal, decontamination and sale as is. Although risk assessment could be used in two categories, disposal and decontamination, only decontamination offers sufficient pathway exposure to warrant risk assessment. Risk management, however, will apply to all aspects of abandonment of NORM contaminated equipment.

Risk management is important since EPA regulations require generator ownership of waste: The so-called cradle to grave approach. Equipment decontamination is straight forward and requires an operator to provide for the disposal of the contaminated materials resulting from the decontamination process. This material usually finds its way to a storage facility such as one of the low level radioactive waste disposal sites or, more recently, being permanently encapsulated in the plugging and abandonment of oil and gas wells. The encapsulation approach has many attractive benefits from a health physics point of view in that it does not concentrate the waste. The maxim for radiation exposure is time, distance and dilution. One wants to minimize the exposure, put the source far from any individual, and dilute it as much as possible. The encapsulation approach for NORM accomplishes all of these goals.

Risks for disposal of contaminated equipment is similar to decontamination unless the equipment can be processed for recycling of its metal content. If it can be recycled, then the ownership of the waste is not kept, but transferred to the recycler. Here, the equipment has value and is being recycled so it is no longer a waste. At the present time, only one facility in the United States offers such a service for steel equipment. The material is recycled into nuclear reactor steel containment structures that must be replaced in nuclear power plants because of structural damage from neutron bombardment.

The sale or transfer of NORM contaminated equipment is not without risk. The problem is that even though a bill of sale is made between two parties where the equipment is identified and documented as to the level of contamination, this does not relieve the initial party from liability since he still has ownership of that part of the waste he originally generated and in theory, could be asked to remediate that portion of the waste.

CONCLUSIONS

In today's environment, managing environmental risks in oil and gas operations are very important to insure success. NORM presents a special type of environmental risk for the oil and gas industry and is further complicated by different state NORM regulations. Risk management can be a useful tool for management of NORM in the oil and gas industry. Risk assessment for NORM requires assumptions, but can provide the risk manager with the necessary objective information to develop effective health physics policies. The use of risk assessment requires one to properly evaluate an operation, identify the NORM source, the worker exposure and the exposure pathway. The next step is to develop an appropriate model with reliable dose-response data and then generate a risk data for the operation. This should be provided to the risk manager along with all of the assumptions that were made for the calculation to address worker exposure levels. The risk manager can develop an acceptable plan with suitable health physics working standards.

During normal operations where NORM is present, it is behind pipe or totally enclosed by pipe or steel and poses no significant health risk. This generally precludes the need for risk assessment. An exception would be where radiation readings in areas of common access would be in excess of exposures allowed by state health physics plans or federal guidelines.

Abandonment of NORM contaminated equipment is complicated and requires the integration of state regulations with risk assessment for the risk manager. Generally, liability and cost issues become the driving factors for risk managers in choosing a particular disposal option.

Although NORM associated with oil and gas operations may have a potential for inducing cancer, there is no direct data to verify this for the levels of NORM exposure currently documented for oil and gas operations and no significant health problems with regard to NORM have been identified. However, the public concern of potential problems

persists and is fueled by public relations blitz which may be appropriate for a group like General Motors that wants to market a product. But I don't think its an appropriate federal role. [23]

Similarly, Rosalyn S. Yalow[21], a celebrated health physicist who was awarded the Nobel Prize in Physiology or Medicine for the development of radioimmunoassay in 1977, has been one of the more vocal critics of policies that attempt to regulate low-level radiation and takes pleasure in challenging them and showing how ridiculous the EPA s radon program is. [22] Yalow points out that many in the scientific community have been quieted by grant money from the EPA and DOE to study the effects of low-level radiation and radon.[22] Indeed, it is difficult to bite the hand that feeds you.

An understanding for the regulatory environment for NORM is difficult but clues can be found by examining our political culture. George Kennan, former diplomat, suggested that Americans should approach world affairs as gardeners and not mechanics.[24] This reflects the common perception that Americans are "preeminently [people] of short view," that they are "compulsive rather than relaxed," and that they "fail to reap the advantages of thoughtful policy-planning." [25] This type of characterization, especially the lack of thoughtful policy planning, begins to explain some of the difficulties in developing effective, sensible and prioritized regulations that address real problems.

An EPA official who requested anonymity, best summarizes the question:

> "I guess the basic philosophical question is how intelligent is the American public. Can the American people handle different options-can they handle the fact that risks are uncertain? Or do we have to speak to them on a third grade level, so prescriptively that we almost take on an Orwellian big brother attitude." [23]

For the oil and gas industry, regulatory requirements for NORM will add burden to a struggling industry without ever addressing the risks of the economic impact to an area or the country for lost jobs and income from the costs associated with such regulations. One is left with the need to proceed with the management of a risk that can not be accurately quantified due to its very low values, when other risks such as smoking, which can be adequately quantified are not addressed or regulated. Science and facts so far have limited value in addressing regulatory issues.

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NORM WASTE TECHNOLOGIES USED IN DECONTAMINATION & WASTE HANDLING: AN OVERVIEW

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INTRODUCTION

The presence of NORM (naturally occurring radioactive material) in crude oil and natural gas has been recognized since the 1930s. NORM forms when small quantities of radium and uranium precipitate with barium and calcium as carbonates or sulfates. In the early 1980s, the oil and gas industry expressed concern that NORM scale, which accumulates in well tubing and processing equipment, and which often contains elevated levels of radium, can represent a source of radium exposure to workers. The greatest hazard to humans is the inhalation or ingestion of the material into the body. Radium, which has a half-life of 1,620 years, emits alpha particles which can cause tissue damage.

NORM has been found in every oil producing region in the United States, from Alaska's Prudhoe Bay to the deep, offshore rigs in the Gulf of Mexico, causing a build-up of low level radiation in oil field equipment. The radium leaches from mineral deposits into adjacent water, and is then pumped to the surface with oil. NORM contamination can be a problem wherever scale precipitated in oil production operations can accumulate. The most prevalent radioactive contamination is found in the South and along the Gulf Coast regions, where radium concentrations in the water are much higher than in other regions.

The environmental as well as health and safety issues attendant to NORM in the oil and gas industry are receiving increased attention from both the public and private sectors. Although regulation of NORM in the United States is only emerging at this time, there appears to be a groundswell of state NORM regulations on the horizon. As a result of the enhanced regulatory climate and the proactive environmental mindset of the oil and gas industry, several major and independent oil and gas companies are in the process of cleanup and ultimate disposal of NORM.

SURVEY / IDENTIFICATION

NORM concentrations vary from background levels to levels exceeding those of some uranium mill tailings. The abundance of NORM concentrated in equipment and soil media is dependent on many factors including the amount of uranium and thorium present in the subsurface formation, formation fluid chemistry, extraction, treatment, and secondary retrieval processes, as well as age of the production field (API,1992).

The most common way to identify NORM contamination is to utilize radiation survey instruments. The presence of NORM can be observed using an external gamma exposure survey meter such as a calibrated scintillation detector. This instrument measures the gamma rays that are emitted from a radioactive source in counts per minute [cpm], microroentgen per hour [μR/hr], or microrem per hour [μrem/hr].

NORM contained within equipment or tubulars is regulated by external gamma exposure readings since the radioactive media cannot be directly sampled. Soil media (scales, sands, soil, sludge, etc.), fluids (produced water, process water, etc.) and air are regulated by radioactive concentrations (activity levels measured in picoCuries per gram [pCI/g] or picoCuries per liter [pCi/l]) determined by laboratory sample analysis. An external gamma exposure survey meter may be used to determine a "screening action level" for soil media contamination sampling. Although radioactive concentrations and gamma exposure readings are interrelated, it is difficult to predict the radioactive concentration of soil media from gamma measurements due to self shielding, encasement (metal wall, etc.) shielding, and NORM distribution (API, 1992).

In most states (Louisiana, Mississippi, Texas and Arkansas), NORM regulations govern NORM soil media contamination by both radium concentration and radon flux. A radon flux measurement is described as the amount of radon emanating from a known amount of area at a given time, in units of picoCurie per meter squared per second (pCi/m^2-sec). The radon flux "action level" is set at 20 pCi/m^2-sec for most state regulations. The regulations maintain that if the radon flux is less that the action level, and the average radium soil concentration does not exceed 30 pCi/g, the soil media is not regulated and can be released for unrestricted use. The regulations further state that if the radon flux exceeds the action level, the average radium soil concentration can not exceed 5pCi/g to be eligible for unrestricted use.

The measurement of radon flux in a field environment can be accomplished using large area-activated charcoal canisters (LAACCs) following EPA Method 115 protocol (40 CFR Part 61).

DECONTAMINATION / REMEDIATION

Once equipment or soil media has been identified as regulated NORM, the next step is to remove the contaminated material from its carrier. Remediation of NORM contaminated soil media may include operations as small as using a shovel and pick to larger operations where back hoes and front-end loaders are involved. Soil media is monitored with radiation instruments to determine effectiveness of remediation efforts. A thorough evaluation and pre-characterization of the NORM contamination found in the soil media must be performed in order to effectively estimate the extent of the remediation operation.

Decontamination operations on equipment is less complicated than remediation operations in that the NORM is usually encased inside the equipment and in most cases the NORM material in the equipment can be decontaminated and the waste can be processed within a controlled area.

The control of radioactive material is the primary concern in decontamination operations. Vital contamination controls such as containment areas, pollution/spill constraints and appropriate postings are implemented prior to any decontamination operation. A permanent cleaning facility equipped with an engineered containment area (i.e. concrete slab with side walls), readily available trained man-power, and reliable equipment serves as an excellent prospect for superior contamination control operations.

An efficient and environmentally safe alternative to a permanent facility may be a self-contained marine or land-transportable decontamination operation on or near the location where the NORM contaminated equipment is located. The mobile cleaning operation avoids shipping costs of contaminated equipment and containerized waste for the customer. The decontamination operation is conducted on the customer's property where the entire operation can be monitored by company representatives.

Vessels/Tanks

When the vessel/tank needs to go back into service or cannot be cut up, confined-space entry equipment is required for NORM cleaning operations. If the equipment can be scrapped, the vessel/tank can be made a nonconfined space area by carefully cutting away panels and decontaminating the panels. Tangent NORM material (i.e. scale, sand, sludge) from contaminated tanks and vessels can be directly removed using shovels and rakes, vacuuming and pumping. The NORM material can be containerized directly into Department of Transportation (DOT) approved containers. The remainder of the decontamination inside the tank or vessel requires portable or fixed high-pressure washers in order to remove the NORM residue. After removing the NORM using pressure washing, the decontaminated equipment is monitored internally and externally in a low background using a gamma survey meter to determine the effectiveness of the decontamination process. Wipe tests are performed on the interior and exterior of the equipment to verify that no removable contamination is present.

When the equipment passes all of the survey and wipe tests, it is released for unrestricted use.

Gas Plant Equipment

Natural gas production and processing equipment may be contaminated with a thin film of ^{210}Pb plated onto interior surfaces. Lead 210 is the long-lived daughter product of ^{222}Rn. If NORM is associated within the natural gas stream, ^{210} Pb will plate onto pumps, tanks and production lines. Unlike oil production equipment, gas plant equipment is more difficult to detect using gamma survey equipment. The contamination involved with gas plant equipment exhibits primarily alpha and beta radiation which pose less human external gamma exposure threats but are still considered regulated.

Decontamination of gas plant equipment includes chemical cleaning agents, physical grinding operations, or a two-fold heating and washing process. In the heating and washing process, first the material must be heated in order to distort the plating characteristics of the thin film. Immediately following the heat process, high-pressure washing must be administered to the material to remove the plated film. Alpha/Beta radiation detectors are used to verify the effectiveness of the cleaning operation. Wipe tests are performed on the interior and exterior of the equipment to verify no removable contamination is present. When the equipment passes all of the survey and wipe tests, it is released for unrestricted use. Very little NORM waste is generated in gas plant equipment decontamination aside from the micron filters used in the closed loop water filtration system.

Tubular/Pipe

Due to inaccessibility and to the condensed scale buildup observed in most NORM contaminated tubulars and pipe, an internal cleaning mechanism is deployed to effectively decontaminate them. Such mechanisms include high-pressure water lance operations, rotary brush with an air vacuum system, rattling techniquest, reaming and pipe bending operations. A wet lance operation (using pressurized water) is often the most environmentally safe and effective, since this method keeps contaminated dust to a minimum. In both the wet and dry methods, stringent procedures are followed to minimize airborne NORM contamination and maximize worker protection.

After decontamination, the tubular/pipe is monitored internally and externally in a low background area using a gamma survey meter to determine the effectiveness of the decontamination process. Wipe tests are performed on the interior and exterior of the equipment to verify no removable contamination is present. When the equipment passes all of the survey and wipe tests, it is released for unrestricted use.

Chemical Cleaning

Acids and alkalis are sometimes used in decontamination operations to remove and dissolve corrosion products and NORM deposits in hard to get places (i.e. racks and hangers, x-mas trees, valves, etc.) where the equipment needs to go back into service. Near neutral cleaning agents are also available on the market for certain applications. Surfactants and degreasers can be used in conjunction with pressure washing to expedite the decontamination operation. Care is warranted when any chemical additive is introduced into the cleaning operation due to potential volatile reactions with hydrocarbon based substances. An additional operation of neutralizing acids and bases will need to be performed after the decontamination process is completed.

Filtration Systems

A closed-loop water filtration system used to recycle process water is an intricate part of the decontamination operation. Since all process water used in NORM decontamination operations is considered controlled by the regulatory agencies, all water and scale used in the operation must be disposed of appropriately. Since radium particles are not water soluble, the process water is filtered through micron filters to capture radioactive particles suspended in the fluid. After decontamination operations, the filters are containerized as NORM contaminated waste and sent to the client for ultimate disposal. Eventually, the process water is disposed of at a Non-hazardous Oilfield Waste facility.

REDUCTION / MINIMIZATION

Particle Separation

In most instances, NORM is primarily incorporated in fine sands and particles. The larger particles associated with soil (rocks, limestone, shell, etc.) are virtually uncontaminated aside from being associated within the NORM waste. By separating the larger particles using screens and pressure washing, a considerable reduction of waste can be achieved. Some surfactants or degreasers may be added to the system to assist the washing process.

Dewatering

If the NORM waste is destined for low level waste disposal facilities, the water content inside of the containers must be a certain minimal limit. A centrifuge used for dewatering the end product can be combined with an existing volume reduction system to further minimize the waste. Decanting the water after settling can also be used at a lower cost but with less efficiency. Another alternative would be to use fluid stabilizers (Aquaset, Petroset, etc.) to absorb the fluid.

PACKAGING / CONTAINERIZATION

Once NORM waste has been collected from either equipment cleaning operations or site remediation, the management and control of the waste is of paramount importance since worker protection and the health and safety issues must be constantly addressed. The most common way to package or containerize NORM waste is in 55 gallon DOT approved drums. Drums allow for ease of shipping, temporary storage, and stenciled identification of the waste. For even further protection from leakage, drums are typically stored in fiberglass overpacks.

Alternative methods of NORM waste containerization have been engineered primarily to accommodate NORM waste disposal. One popular method used in the oil and gas industry is the "encapsulation" of the waste in steel casing or PVC tubes. Generally 7 inch or larger steel casing is welded on one end, NORM waste inserted by either gravity-fed or shaker-controlled encapsulation units, and the remaining end welded and inspected. Once a sufficient number of casing tubes have been collected to economically warrant a disposal program, the casing is transported to an abandoned well site and strung up and dropped downhole using pre-approved permits for the NORM waste disposal.

Packaging/Storage

Drums, containers, casing and equipment containing NORM should be stored in a secure and ventilated area with limited access. Any NORM storage area should be an appropriately marked restricted area, with access limited to authorized personnel only. Drums, containers and equipment should be inspected periodically and should be immediately repacked or resealed if found to be leaking. All openings on equipment or tubing containing NORM should be capped, plugged or wrapped in plastic when in storage to prevent the spread of radioactive materials. Employers or contractors who enter NORM storage areas should be NORM trained, or at a minimum, informed of the presence of NORM and the safety problems associated with exposure to radioactive materials for worker protection.

NORM storage areas should be identified with signs like "Caution, Radioactive Materials" at all entrances. Drums, containers and equipment containing NORM should be properly tagged or labeled. This label should include identification that corresponds to records of the material. Records and documentation should be maintained pursuant to the existing state NORM regulations and federal DOT regulations.

NORM DISPOSAL

Since there are no federal and few state regulations directly applicable to the disposal of NORM generated in the oil and gas industry, it is recommended that owners/operators/generators of NORM consult applicable state and local regulatory agencies, as well as review lease or landowner rights and obligations before disposing of NORM. It is also recommended that "cradle-to-grave" records and documentation of the types, volumes, radioactive analytical data, decontamination contractors, haulers and destinations be kept in good order.

Listed below are various options and methods for the disposal of oilfield NORM. As the demand for disposal services increase, it is likely that there will be technological advances with increased commercial applications.

1) Plugged and Abandoned Wells

When approved in advance by the appropriate regulatory agencies, well abandonment operations provide an excellent way to dispose of NORM. The popular P&A slogan "let's put it back where it came from" seems to make this method the disposal option of choice in the oil patch. NORM may be placed in identified wells during plugging and abandoning operations using the following procedures:

- Grind, Slurry, Mix & Pump

  NORM gathered from decontaminating tubulars and other production equipment can be ground and mixed with cement slurries and then pumped into a formation or spotted as wellbore plugs for any plugs located below the plug isolating the lowermost underground source of drinking water (USDW). To protect against potential groundwater contamination, NORM should not be mixed with cement slurries used in isolating USDWs, fresh water zones, or in the surface plug.

  NORM waste can also be ground and blended with certain well control fluids and pumped in the wellbore below the lowermost USDW. In this case, the resulting NORM containing fluids should be isolated in the wellbore between cement plugs.

- Dry-hole, Gravity Fed

  This method of downhole NORM disposal is probably the most cost effective to the NORM generator. It simply involves drying the hole first using a nitrogen pumping or other acceptable process and then utilizing a controlled shell shaker apparatus to gravity feed the NORM in the wellbore between cement plugs.

This method also allows the maximum amount of NORM to be displaced in the wellbore since there are no fluids or additives enhancing the total NORM waste volume. The caveat to this method is the control and rate of the feed of NORM downhole so as to prevent the possibility of any bridging over.

- Encapsulation

NORM waste, tyvek suits, plastic or other contaminated media can be "encapsulated" or containerized in tubulars or casing (casing is typically better since the I.D. is generally larger) by placing the material inside the casing using various above ground and subsurface encapsulation methods. Once encapsulated, the NORM may be disposed of by stringing up the tubulars or casing and dropping them in the wellbore using proper plugging and abandoning procedures.

- NORM-Contaminated Tubulars

Some state regulatory agencies will allow NORM-contaminated tubulars to be installed beneath or between all plugs in the wellbore or cemented in place within a full cement column. In these cases, a plug is generally set in the casing above the top joint of tubing. In any event, NORM-contaminated tubulars should not be left in the wellbore at depths above the lowermost USDW so that the potential for ground-water contamination does not occur.

2) Well Injection and Hydraulic Fracturing

NORM wastes can be mixed using mud or cement and then injected or fractured into formations which are isolated geologically from USDW's. In order to ensure compatibility, generators must evaluate formation and injection fluid characteristics prior to the injection of any NORM wastes. To date, most commercial application of well injection and hydraulic fracturing has been done using candidate wells offshore.

3) Licensed NORM Waste Disposal Sites

Commercial NORM waste disposal sites or landfills fall under the jurisdiction of both the state agencies in which they are located and the EPA, whose regulations define a NORM waste disposal site for disposal of uranium and thorium mill tailings and related byproduct materials (40 CFR, Part 192). These sites are designed to contain NORM and other byproducts for long periods of time and, after closure, are typically deeded back to the state for permanent monitoring and restricted future use. The key, therefore, to choosing such a facility to dispose of NORM waste is the amount and viability of the facility's escrow fund for the perpetual care and maintenance of the landfill.

4) Smelting

Smelting may be a viable disposal option for NORM-contaminated tubulars or other oilfield equipment with higher radium concentrations. Basically, when NORM-contaminated equipment is smelted, residual NORM accumulates primarily in the resultant slag. Although not commercially applicable at this time, smelting studies are ongoing.

5) Land Spreading with Dilution

This method of NORM disposal basically involves the mixing of scale or sludge with non-NORM soil and spreading on the surface of open lands where NORM was not originally present above background levels. State regulatory agencies have approved such a "treatment facility" at a non-hazardous oilfield waste (NOW) site in Louisiana, however, a lawsuit has been filed challenging the agency's approval procedures. At the time of this writing, construction of the NORM treatment facility in Louisiana was not complete.

NORM Disposal Options

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Abstract

NORM (Naturally Occurring Radioactive Material) is a rapidly emerging issue associated with oil and gas production, as well as chemical and petrochemical processing. NORM awareness is growing with spreading state and potential Federal regulation. As of October 31, 1993, five states and one area have promulgated NORM regulations and were struggling with new interpretations (Texas, Louisiana, Mississippi, Michigan, Arkansas, Offshore Gulf of Mexico). It is estimated that at least twelve additional states will have NORM regulations by the end of 1994. disposal of NORM wastes has not been racing down the regulatory path, as fast as the licensing process. Formidable problems arise in the arena of low level radioactive wastes, which include NORM wastes. Disposal solutions are complex and involve a cross-section of technical and social problems that could last thousands of years. For example, since ^{226}Ra has a half-life of 1,602 years, and any ^{226}Ra we dispose of today will still have more than half of its original activity more than a millennium from now. Disposal planning must face this troubling fact with a sense of future social and environmental prudence and scientific prediction.

Introduction

NORM (Naturally Occurring Radioactive Material) is a rapidly emerging issue associated with oil and gas production as well as chemical and petrochemical processing. NORM awareness is growing with spreading state and potential Federal regulation. At the time of this writing (October 31, 1993) five states and one area have promulgated NORM regulations and were struggling with new interpretations. These states include the following:

Texas	Offshore Gulf of Mexico
Louisiana	Michigan
Mississippi	Arkansas

It is estimated that at least twelve additional states will have NORM regulations by the end of 1994.

Disposal of NORM wastes has not been racing down the regulatory path as fast as the licensing process. Disposal of low level radioactive waste presents some formidable problems now that NORM's Pandora's Box has been opened. Disposal solutions are complex and involve a cross-section of technical and social problems that could last for thousands of years. For example, Radium-226 (^{226}Ra) has a half-life of 1,602 years and is part of a decay series that ranges from 4.5 billion years to 1.5×10^{-4} seconds. In other words it just continues to be radioactive over a very lengthy time frame. Disposal planning must face this troubling fact with a sense of future social and environmental prudence and scientific prediction. This radioactive permutation is unlike any other

found in site planning.

Disposal Site States

Presently there are only four states that have sited NORM disposal landfills and/or landfarms. These are listed below in the following table:

State	Number & Type	Company	Location
California	Landfills (5) private	Public Utility	Unknown Imperial Valley?
*Utah	Landfill (1)	Evirocare	Clive
*Washington	Landfill (1)	U.S. Ecology	Richland
Louisiana	Landfarm (1)	Sanifill	Campbell Wells

* At the time of this writing, these are the only commercially available landfills (October 31,1993).

The Minerals Management Service (MMS) became involved in the NORM disposal issue in 1988 when an offshore operator applied for permission to inject NORM into a depleted reservoir. The MMS issued interim guidelines concerning the disposal of NORM in December, 1991. The preferable method according to the MMS is slurry encapsulation in a well to be permanently abandoned. A second method is to dispose of NORM by downhole injection into an isolated permeable formation between shale sections (a shale sandwich). Following injection, the well is to be plugged.[2] The MMS requires extensive geologic and environmental information as essential ingredients to any disposal method. Overboard disposal was allowed at certain levels of NORM

contaminated materials, but this is no longer an option.

It can be seen from the table presented above that disposal options are at present very limited. The American Petroleum Institute (API) has recommended downhole injection as a viable option either offshore or onshore. However, the most common method today practiced by operators is encapsulation in short pieces of PVC pipe, mixed with a slurry of cement and plugged in a permanently abandoned well. Class II injection wells have not been approved for an on-going program of injection with produced brine water. No one has figured out how to inject a NORM contaminated 12" valve in 5.5" casing to this date.

NORM Disposal in Texas

In most states NORM disposal and licensing is administered by a central environmental agency. Texas has taken a different route and divided the whole thing into three agencies. **First**, the licensing and action levels are handled by the Texas Department of Health, Bureau of Radiation Control. **Second**, the Texas Railroad Commission has been given the task of NORM disposal associated with oil and gas field operations and must promulgate regulations in the near future. **Third**, the Texas Natural Resources Conservation Commission (formerly the Texas Water Commission) has been given the stewardship of NORM disposal other than oil and gas field waste. It may be advisable to site only one landfill in this tri-parte process, however confusion is beginning to permeate the nooks and crannies of NORM issues in Texas, as might be expected. It is understood that "Memorandums of Understanding" are being drafted between the three

agencies at the time of this writing.

Exploration and Production Wastes

Produced water is by far the largest and most voluminous waste problem associated with oil and gas production. The United States produces about 2.5 billion bbls of oil each year and about 21 billion bbls of associated brine water. The brine water transports the NORM related radionuclides from the reservoirs and deposits scale and sludges in the tubing and production equipment. This is the prime origin of NORM, but other sources exist in a gas and vapor phases. The four radionuclides involved most extensively with oil and gas production are as follows:

^{226}Ra -70 %	Radium
^{228}Ra -30%	Radium
^{210}Pb	Lead
^{222}Rn	Radon

Radium is in the same chemical category or group as Calcium, Barium, Strontium, Beryllium and Magnesium. These elements often associated together to form silicates, carbonates and sulfates. Thus barite ($BaSO_4$) is often associated with Radium and deposited as a scale. More complex molecules are also found. One of the puzzling questions is the barite used in drilling mud a catalyst for concomitant radium deposition at a later stage of production or is NORM totally derived from fossil brine water ?

NORM Processing and Disposal Options

A distinction should be made between NORM **disposal processes** and NORM **disposal options**. The "processes" involve volume reduction, abatement and encapsulation of NORM waste. The "disposal" options review the places where the NORM processed waste can be stored for long periods of time or returned to the origin of NORM.

Disposal processing encompass the ways and means of volume reduction and packaging. New methods are being introduced on an experimental basis in rapid fire succession.

The following is a partial list of these methods. Many variations continue to evolve from this list.

Compaction -	volume pore reduction through crushing and de-watering.
Encapsulation -	volume division into discrete containers, such as short lengths of PVC pipe.
Vitrification -	volume reduction and encapsulation melted and fused into glass bullets
Drums & Cement -	packs of equipment, scale and sludge into cement filled drums

Soil Washing - volume reduction of NORM waste through soil washing and mechanical screening.

Particle Reduction - grinding and sieving scale and sludge to fine grain sizes which will pack into smaller volumes and enable injection into well bores.

Disposal options are also varied and pose varying environmental risks dependent upon the method of disposal. The following list is arranged in an order that reflects the highest environmental risk to the lowest.

Higher Risk	1	Landfarm or Landspreading
	2	Landfill
	3	Throw it overboard (at sea)
	4	Store low volumes on site
	5	P. & A. Wells with NORM waste slurries
	6	Salt Domes
	7	Class II Injection Wells
	8	Class I Injection Wells
Lower Risk	9	Bedded subsurface salt mines

The two most common practices utilized today are landfills and plugged wells. It is suggested in this paper and it has been suggested in other papers[3,4] that Class II injection of NORM processed scale and sludge is the most cost effective and environmentally safe disposal option that exists to date. The caveat that might be added is that this type of Class II well should be highly regulated as to record keeping, integrity testing, plugging procedures and deed records. There are long term ownership implications involved in thousand -year NORM waste sites. All of the options must consider the environmental consequences for future generations. Deed records should reflect the continuing social and owner responsibility for any of the disposal options. For example, who will take the responsibility for the integrity of a 300 year old casing failure and the potential contamination consequences of a slurry plugged well that failed to inject the NORM into the formation in such a manner that the fractures could naturally collapse around the NORM waste and encapsulate it in time and space ? Is it the landowner or the state or the county or the nation ? Most plugged wells have a casing life that may vary from months to several hundred years. Will they last 1,602 years? The obvious answer is negative, thus setting the precedent and argument in favor of fracture-induced injection in Class II injection wells.

Disposal Costs

Disposal costs are highly variable and dependent upon the following factors:

Processing options

Waste reduction

Disposal method chosen

Shipping costs

Increasing competition

Regulatory requirements

Public awareness, ignorance and fear

Litigation

At the present time disposal costs may vary from negligible to $1,800.00 per drum. Most operators and owners would prefer the negligible end of the spectrum but it is not often the most prudent or possible course of action due to regulatory restrictions and potential litigation.

NORM Radioactive Half-Life and the Uranium-238 Decay Series

The origin of NORM begins with a unique set of radioactive decay steps that begin with either Uranium, Thorium or Actinium. This paper will only consider the Uranium -238 Decay Series to illustrate the concept of half-life as it relates to disposal responsibility and courses of action. The following table depicts the ^{238}U Decay Series with associated half-life. Each element created has a unique half-life which requires about seven half-lives to completely be transformed into another radioactive element and finally to a non-radioactive stable element.

Element	Half-Life	Decay to New Element
Uranium-238	4.5 billion years	Thorium - 234

Thorium - 234	24.1 days	Protactinium - 234
Protactinium - 234	147 days	Uranium - 234
Uranium - 234	2.5×10^5 years	Thorium - 230
Thorium -230	7.5×10^4 years	**Radium - 226**
Radium - 226	**1602 years**	**Radon - 222**
Radon - 222	**3.83 days**	Polonium - 218
Polonium - 218	3.05 minutes	Astatine - 218
Astatine - 218	2.0 seconds	Lead - 214
Lead - 214	26.8 minutes	Bismuth -214
Bismuth - 214	19.7 minutes	Polonium - 214
Polonium - 214	1.5×10^{-4} seconds	Thallium - 210
Thallium -210	1.32 minutes	**Lead - 210**
Lead - 210	**19.4 years**	Bismuth - 210
Bismuth - 210	2.6×10^6 years	Polonium - 210
Polonium- 210	138 days	Thallium - 206
Thallium - 206	4.23 minutes	Lead - 206 (stable)

It can be seen from the ^{238}**U Decay Series Table** that half-life ranges from nano-seconds to billions of years. However, the primary constituents of NORM fall within the hundreds to thousands of years. For example a gram of ^{226}Ra will take 7 x 1602 = 11,214 years to completely decay to ^{222}Rn gas. This is the time frame magnitude that should be considered in reaching for the most cost effective and environmentally sound disposal method.

The Best Options

The best options are to learn more about NORM radionuclides and their geological, hydrodynamic, hydrogeological and geochemical pathways, correlations and reactions. Very limited or practically no correlations have been made between NORM and the geologic ages, paleoenvironments of deposition, lithology, drilling fluids, production rates, brine chemistry, kerogen chemistry and a host of other factors that remain un-named and classified. Volumes of correlative research are sorely needed along with raw data. This will evolve through time through the natural process of regulation. The author is calling for a more concentrated effort by industry, Federal and state governmental agencies. It will become a necessity to address the disposal and waste reduction issues in the next few years with a substantial data base.

Expedient and Safe Options

It is obvious that several disposal options will necessitate the handling of NORM contaminated equipment along with scale and sludge. Landfill will obviously be a short term solution for equipment that cannot be cleaned or decontaminated. An alternate and more preferable solution for equipment would be burial in bedded salt, such as the WIPP (Waste Isolation Pilot Plant) in New Mexico[1] or a similar site.

The most preferable method for scale and sludge is fractured or permeable injection into the deep (5000 - 10,000 feet) geological formations. The ultimate lithostatic and hydrostatic pressures will ensure encapsulation through geological processes by healing the induced fractures or confining permeable beds between a "sandwich" of

thick shales. Injection into the shales is also an option. Plugging procedures could include allowances for natural forces to collapse the hole between plugs ensuring not only formation encapsulation, but hole encapsulation as well, again through natural geological forces. The author suggests that a great number of the Class II salt water injection wells would qualify for NORM injection wells. Strict, sane and scientific regulation should accompany these NORM injection wells along with deed recording. NORM should be returned to it's origin as Nature provided the ultimate disposal option aided by owners and operators.

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1 Wilson, W. F., NORM, A Guide to Naturally Occurring Radioactive Material, 250 pages, PennWell, 1993.

2 Rutherford, G.J., Richardson, G.E., Disposal of Naturally Occurring Radioactive Material on Federal Leases in the Gulf of Mexico, p 101-110, SPE 25940, Environmental Conference Proceedings, March, 1993.

3 Lowe, D.J., NORM Cleaning and Disposal Using Closed-Loop Hydroblasting or Solvent Bath and Underground Injection, p 77-81, SPE 25395, Environmental Conference Proceedings, March, 1993.

4 API Production Department, Management of Naturally Occurring Radioactive Material (NORM) in Oil and Gas Production, Bulletin E2, 1992.

NORM Disposal Options

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Regulated States

October 1993

- Texas
- Arkansas
- Louisiana
- Mississippi
- Offshore Gulf of Mexico

Strata

States Drafting Regulations

December, 1993

- Kentucky
- California
- New Mexico
- Oklahoma
- Alabama
- Michigan
- Illinois
- Pennsylvania
- New Jersey

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Disposal Site States

Landfills or Landfarms

- California (5) **
- Washington (1) *
- Utah (1) *
- Louisiana (1)

- * Available January, 1993
- ** Private landfills

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Texas Disposal

Divided Responsibilities

- Licensing - Texas Department of Health
- Oil & Gas Disposal - Texas Railroad Commission
- Other NORM Disposal - Texas Natural Resources Conservation Commission (TNRCC)

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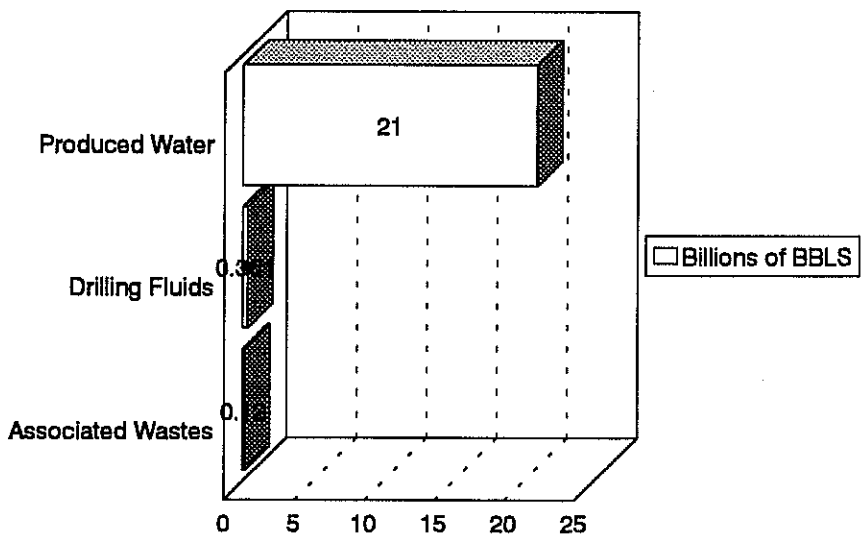
Exploration & Production Wastes

API Annual Estimates - Billions of BBLS



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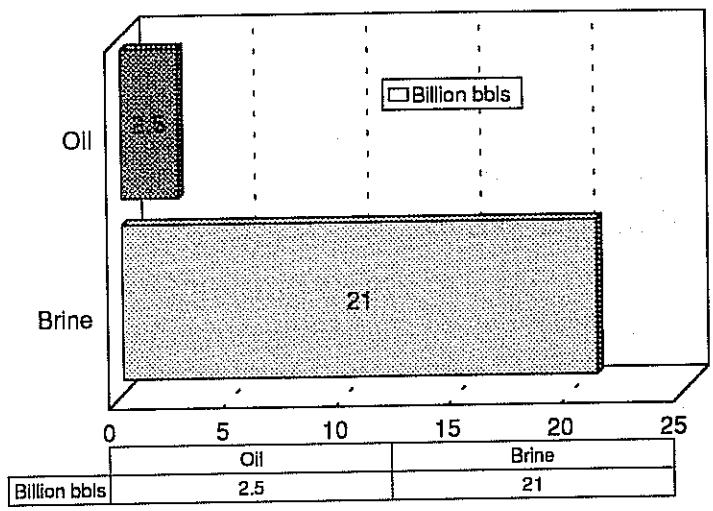
Oil & Brine Water Production

Annual Estimates (U.S.)



Billion bbls	Oil	Brine
	2.5	21

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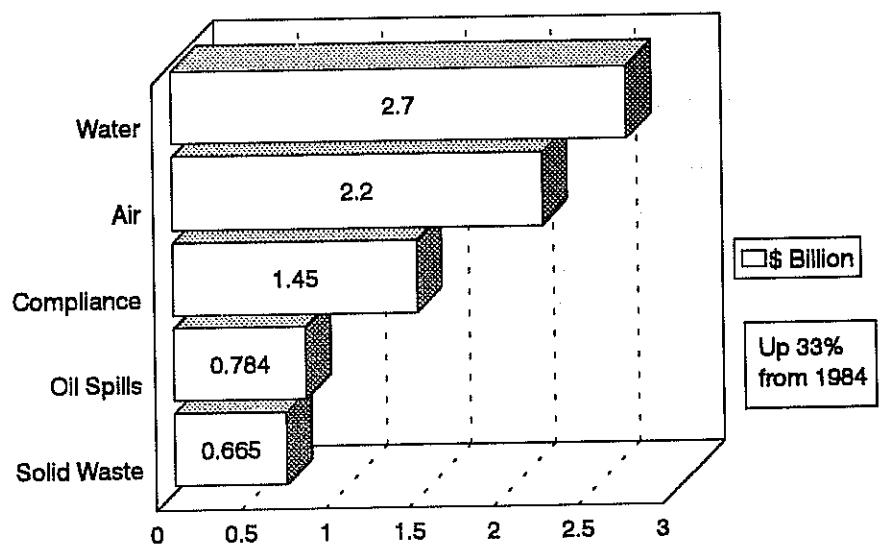
1990 Oil & Gas Environmental Spending

API Data



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Disposal Options

- Landfill
- Landfarm or Landspreading
- Class I Injection Wells
- Class II Injection Wells
- Salt Domes
- Bedded Salt
- NORM P. & A. in Orphan or Depleted Wells
- Store on Site

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Disposal Processing

Volume Reduction

- Compaction
- Encapsulation
- Vitrification
- Drums and Cement
- Mechanical Soil Washing Concentration
- Particle Reduction

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Disposal Costs

- Highly variable and dependent upon :
  - Processing options
  - Waste reduction
  - Method chosen
  - Shipping costs
  - Competition
  - Litigation
  - Public Fear and Ignorance

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Disposal Costs (cont.)

- Today disposal costs vary from about $600 - $1800 per drum - total costs.
- American Ecology - Washington State - $37 per cubic foot
- Envirocare - Utah State - $40 per cubic foot

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NORM Radioactive Half-Life

- Radium - 226 1602 years
- Radium - 228 5.76 years
- Lead - 210 22.3 years
- Uranium - 238 4.5 billion years

- Rule of thumb - 7 half-lives to decay completely to new element

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Uranium - 238 Decay Series

- Uranium - 238 decays to 16 radioactive isotopes prior to reaching stable lead.
- Time of decay varies from 4.5 billion years to 1.5 E-4 seconds.
- Dealing with seconds to billions of years.
- Prime constituents of NORM range across thousands of years.

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Landfill Options

- Pros
  - Low cost
  - Known technology
  - Geological controls
- Cons
  - Public ignorance and fear
  - Half-life problems
  - Political siting versus geological siting

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Landfarm or Landspreading

- Pros
  - Low cost
  - Known or emerging technology (bio-concentration)
  - Dilution solution
- Cons
  - Public ignorance and fear
  - Half-life problems
  - Only can handle low levels of NORM

Strata

P. & A. Wells

- Pros
  - Many wells to utilize
  - Known slurry technology
  - Relatively low costs
- Cons
  - Life of casing 40-50 years
  - Half-life problems
  - Out-of-Site, Out-of- Mind
  - No long term monitoring requirements

Strata

Site Storage

- Pros
  - Very low cost
  - Able to monitor for long periods
  - No public interference
- Cons
  - Temporary solution
  - Regulatory limits
  - Volume problems
  - Lease and ownership problems

Strata

Class I Injection Wells

Hazardous Waste Wells

- Pros
  - Injected into deep subsurface strata
  - Highly regulated and studied
  - No half-life problems
- Cons
  - Only about 700 wells available
  - Relatively high costs
  - Need long term monitoring regulations

Strata

Salt Domes

- Pros
  - Large number of available sites
  - Easily mined
  - Known technology
- Cons
  - Some domes are still moving
  - Half-life problems
  - Public ignorance and fear

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Bedded Salt

- Pros
  - No half-life problems
  - Excellent preservation
- Cons
  - Public ignorance and fear
  - Relatively high costs
  - Limited number of sites

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Class II Injection Wells

Salt Water Disposal Wells

- Pros
  - Large number of wells - 170,000
  - Known technology
  - Near the origin of NORM
  - No half-life problems
- Cons
  - Patchwork of adequate regulation
  - Allowed only offshore by the MMS
  - Public ignorance and fear
  - Environmental professional ignorance and fear

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The Best Options

- Learn more about the genesis of NORM
- Learn more about the correlations of NORM with geology
- Learn more about the correlations of NORM with hydrodynamics and hydrogeology
- Learn more about the correlations of NORM with drilling and completion fluids

- Use this information to abate NORM before it becomes a problem for disposal

Strata

Expedient and Safe Option

- Class II Injection Wells
  - NORM scale and sludge can actually be injected into thick shales and brine bearing sands under pressure. The hydro-fracturing of the formations at depths averaging one mile or more below the surface ensures long term geological encapsulation.
  - NORM is returned to it's natural origin.
  - Will require carefully crafted regulation, long term monitoring, and deed records.

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Dual Solutions

- It is a little difficult to inject a 12" valve into 2 7/8" tubing
- Must develop a dual system of NORM disposal
  - Geologically correct landfills and new processing
  - Class II Injection wells

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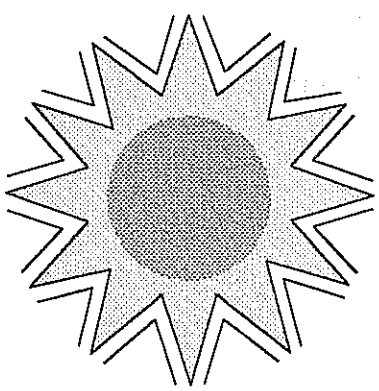
The Final Solution

- Send it back to the Sun



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Characterization of NORM Vessel Solids

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Vessel solids (tank bottoms and separator sands) from the Gulf Coast region of the United States are typically comprised of fine to very fine sand and silt sized particles. These particles are predominatly a mixture of quartz, barite, and amorphous iron oxides. Barite in these materials is present as isolated precipitates on grains, grain coats, and as fine to very fine sand sized particles. Vessel solids can be substantially radioactive due to the co-precipitation of radium (Ra) with barite. Both uranium (U) and thorium (Th) are also present in these materials. When present, U is at crustal abundance relative to silicon (Si). Th, in contrast, is present above crustal abundance levels with respect to Si (~ x 3.5). In addition to Ra, vessel solids can contain substantial levels of zinc (Zn), lead(Pb), copper(Cu), and arsenic (As). Due to the small size, ease of communition, and sometimes intimate association with inert materials, removal of Ra contaminated barite from these solids by simple physical means is extremely difficult. The simplest means to reduce the volume of this waste stream is fluid removal. Removal of fluids (oil and water) from this waste stream would reduce waste volume by approximately 45%.

Introduction

Recent regulatory action in Louisiana and contemplated regulatory action in other states and at the Federal level have focused considerable attention on NORM (naturally occurring radioactive materials) in oil field wastes. Experience to date in Louisiana has shown that processing and disposal of NORM waste is expensive. Technology is needed that will safely and cost effectively provide for the handling of NORM contaminated wastes. A necessary pre-condition for the development of waste handling technologies is detailed knowledge of the waste stream to be handled. NORM wastes have been the subject of a number of recent studies (e.g. Otto, 1989; ; Rogers, *et. al.*, 1989; Baird, *et al.*, 1990), but none of these studies has provided detailed waste characterization data. Moreover, most studies have focused on pipe scales. Here, detailed chemical, physical, mineralogical, and radiochemical information is presented concerning the nature of an important NORM waste stream component, vessel solids (separator sands and tank bottoms).

Background

The recognition that natural materials can emit ionizing radiation dates from Becquerel's observations of the effects of uranium rich minerals on covered photographic plates (Becquerel, 1896) and the isolation of polonium and radium from pitchblende by the Curies (Curie, Curie, and Bemont, 1898). Knowledge of the presence of natural radioactive substances in association with hydrocarbon production dates from the early 20th century when radon was found in some Canadian natural gases (Satterly and McLennan, 1918). Since then, numerous workers have observed elevated levels of actinide decay series elements in oil, natural gas, pipe scales, and vessel solids (separator sands and tank bottoms). Published reports of these occurrences are available for the United States, the North Sea, and Russia (Anderson, 1990), but the ubiquity of U and Th in the earth's crust suggest that Ra bearing scales will be common wherever produced water is salty, hot, and depleted in sulfate (Kraemer and Reid, 1984). The primary radioisotopes of interest in these so called NORM (naturally occurring radioactive materials) contaminated materials are ^{226}Ra and ^{228}Ra in pipe scales and vessel solids, ^{222}Rn in natural gases, and ^{210}Pb and ^{210}Po deposits in natural gas handling equipment.

The widespread occurrence of actinide decay series elements is not suprising. Both parental elements, U and Th, are relatively abundant in earth solids. On a whole earth basis, U (18 ppb) and Th (65 ppb) are comparable in abundance to materials perceived as reasonably common (i.e. indium (2.7 ppb), thallium (4.9 ppb), mercury (9.9 ppb), iodine (17ppb), cadmium (21 ppb), tantalum (29 ppb), beryllium (56 ppb), cesium (59 ppb), rhenium (76 ppb), silver (80 ppb), and

bromine (135 ppb) (Ganapathy and Anders, 1974). Both U and Th are lithophilic elements, and consequently, both are substantially more abundant in the earth's crust than in the earth as a whole (crustal abundance: U = 2.7 ppm; Th = 9.6 ppm) (Taylor, 1964). Moreover, both U and Th are sometimes greatly concentrated in some sedimentary rock types (shales, coals, phosphatic rocks, some limestones, and some sandstones). Because of their chemistry, however, neither U nor Th are typically mobilized from hydrocarbon reservoirs and concentrated in scales and sludges. In contrast, their Ra and Rn decay daughters are mobilized from hydrocarbon reservoirs. Gas streams contain Rn and gas handling equipment can become increasingly radioactive from the accumulation of ^{210}Pb and ^{210}Po, relatively long-lived ($t_{1/2}$ =22 yr and $t_{1/2}$ =138 d, respectively) decay daughters of ^{222}Rn. Mineral scales and sludges, particularly barite ($BaSO_4$), precipitated from produced water can become quite radioactive due to incorporation of ^{226}Ra ($t_{1/2}$ ~ 1600 yr) and ^{228}Ra ($t_{1/2}$ ~ 6 yr); decay daughters, respectively, of ^{238}U and ^{232}Th. If produced water is discharged into earthen pits, as was sometimes past operating practice, soil in the pits may become contaminated with Ra, as an exchange cation on clays, as a constituent in $BaSO_4$, and, possibly, otherwise.

Materials and Methods

This study considered 17 samples of vessel solids were collected from separators and tanks in onshore and offshore settings (southern Louisiana and western Gulf of Mexico area, respectively). Materials for study were selected on the basis of positive survey meter readings. These materials were subjected to extensive visual, physical, chemical, mineralogical, and radiochemical analysis. Analyses performed and methods used are given in Table I.

Results and Discussion

Analytical results obtained for the vessel solids are given in Tables II through V. As received (Table II), these materials contained, on average, 5.52 wt. % oil, 15.97 wt. % water, and 78.51 wt. % solids, and had the consistency of relatively gritty, fluid, peanut-butter. The particles comprising these solids were fine to very fine sand and silt particles. On average, 22.58 wt. % of the particles were coarser than 180 μm. The average median grain size of particles finer than 180 μm was 26.20 μm, and half of all particles finer than 180 μm were between 10.77 and 39.44 μm in diameter. The mineralogy of the samples was dominated by quartz and barite with infrequent and minor occurrence of calcite, celestite, bassinite, calcium rich albite (calcium content not determined), ferroan dolomite, and pyrite. Iron rich phases present in the solids were typically amorphous. The average bulk composition of the solids (major constituents only, Table III) was 46.92 wt % SiO_2, 19.23 wt. % $BaSO_4$ + $SrSO_4$ (overwhelmingly $BaSO_4$), 4.67

wt. % Fe_2O_3, 2.36 wt% FeO, 2.13 wt. % CaO, and 1.73 wt. % Al_2O_3. The large loss on ignition fraction (average 6.41%) reflects the highly organic and sulfur rich nature of the samples. Minor constituents (Table IV) of note include Zn, Pb, Cu, and As, which, respectively had average concentrations of 3400, 2804, 302, and 151 ppm. The leachability of these constituents was not determined. It should be noted that the analytical results for these samples do show lack of mass balance in a number of cases. This may be due to volatilization losses during production of the glass bead for XRF analysis; as reported in Table III, the results have not been normalized to 100%.

The samples (Table V) had reasonably high levels of both ^{226}Ra (average activity 62201 pCi/g (picoCuries/gram = 10^{-12} Curies/ g); median activity 2142 pCi/g) and ^{228}Ra (average activity 8867 pCi/g; median activity 560 pCi/g). The highest activity samples contain 10-100 nCi/g (nanoCuries/gram = 10^{-9} Curies/gram) levels of Ra and are similar in activity to the highest activity scales described from southeastern Kansas by Gott and Hill (1953). Although, the activity of both Ra isotopes is not necessarily correlated with barite content, there is a general pattern of increasing Ra content with increasing Ba+Sr content (see Fig. 1) All samples are substantially higher in ^{226}Ra activity than ^{228}Ra activity (minimum ^{226}Ra:^{228}Ra activity ratio of 50). Observations by Kraemer and Reid (1984), and our laboratory, of ^{226}Ra:^{228}Ra in Gulf Coast region produced waters indicate that freshly precipitated barite should have a ^{226}Ra:^{228}Ra ratio of between ~ 0.4 and 1.2. The ^{226}Ra:^{228}Ra values obtained for these samples show a very strong depletion in ^{228}Ra relative to ^{226}Ra. This could be due to age of the vessel solids. If the ^{228}Ra in this barite is not renewed by equlibrium exchange with produced water, it will decay to low activity levels much faster than ^{226}Ra. The ratio of ^{226}Ra to ^{228}Ra could be used as a geochronometer which would provide an estimate of the "mean" time since the Ra bearing phase was in equilibrium with produced water. Unfortunately, this would not be a very accurate geochronometer. It's application would require accurate knowledge of the equilibrium ^{226}Ra / ^{228}Ra ratio in the solids, and it would be necessary to account for Ra isotopes generated *in situ* by included U and Th.

The samples show an average Ba:Sr mole ratio of 16.92, but the samples displayed a wide range of Ba:Sr mole ratios, from as Sr enriched as 5:1 to as Ba rich as 60:1. As shown in Fig. 2, there appear to be two populations of $BaSO_4$ materials. In one population, there appears to be a relationship between increasing mole fraction of Sr with respect to barium and increasing Ra isotope activity. In the other population, the activity of Ra isotopes appears to be unrelated to the ratio of Ba:Sr.

The vessel solids samples consistently contained Th (average 40 ppm), but U was found above its detection limit in only four samples (4 ppm concentration maximum). Based on the calculated averages shown in Table V (which do not include those values reported as below detection), the U:Si ratio is approximately that expected for crustal rocks. If the below detection values are

taken into account (either as nulls or as the numeric value of the detection limit), U would be considered as depleted with respect to normal crustal rocks.
In contrast, the Th:Si ratio shows substantial enrichment with respect to crustal rocks (on average by a factor of ~ 3.5). Neither ^{226}Ra nor ^{228}Ra activities appear to vary in response to either Th or U concentration. This lack of association indicates that the activities of Ra isotopes in these vessel solids are not supported by either U or Th.

Barite is present in these vessel solids in two distinct geometric arrangements. SEM photographs of two typical vessel solids samples are shown in Figs. 3 and 4.. Fig. 3 shows a barite poor sample. Fig. 4 shows a barite rich sample. Samples poor in barite are comprised of angular to subrounded quartz grains. In these samples, barite is typically present as grain coats and isolated patches. Samples rich in barite often contain fine to very fine sand sized, angular, massive clasts of barite. Experiments in our laboratory have shown that physical separation of radium contaminated barite from the non-radioactive materials in separator solids is extremely difficult. This difficulty arises for two reasons: First, the discrete barite fragments present are brittle. Consequently, physical agitation of these particles results in grinding and grain breakage with further reduces their size. Second, the barite present as grain coats and isolated patches could not be removed by mechanical action. One interesting finding from these experiments was that the discrete barite particles have a lower Ra:Barite ratio than barite grain coats. The Ra:Barite ratio in the discrete barite particle rich separates was ~1600 pCi/gram barite compared to the mean Ra:Barite ratio for the barite coated quartz grains of ~5400 pCi/gram barite. This result is of no immediate practical consequence to mechanical separation technology; both separates would comprise regulated NORM waste. But this result does suggest separate origins for the two types of barite. The barite coatings and patches on quartz grains probably arise via rapid and not highly selective precipitation. The discrete barite particles probably arise from slower and relatively more selective precipitation.

Although volume reduction of this waste stream by concentration of the radioactive barite by simple physical means is unlikely, a substantial volume reduction might be achieved by removing fluids (oil and water). Based on their densities, the relative average volumetric abundance of fluid and solid constituents in a vessel solids waste stream is ~ 14 % oil, 31% water, 48% inert solids, and 7% Ra contaminated barite. Consequently, simply removing fluids would reduce waste volume by ~45%.

Conclusions

Vessel solids (tank bottoms and separator sands) from the Gulf Coast region of the United States study are typically comprised of fine to very fine sand and silt sized particles. These particles are a mixture of quartz, barite, and amorphous iron oxides. Barite in these materials is present as isolated precipitates on grains, grain coats, and fine to very fine sand sized particles. Vessel solids can

be substantially radioactive due to the co-precipitation of Ra with barite. Both U and Th are also present in these materials. When present, U is at crustal abundance relative to Si, but Th is, on average, present above crustal abundance levels with respect to Si (~ x 3.5). In addition to Ra, vessel solids can contain substantial levels of Zn, Pb, Cu, and As. Due to the small size, ease of communition, and sometimes intimate association with inert materials, removal of Ra contaminated barite from these solids by simple physical means is extremely difficult. Even so, the volume of this waste stream could be reduced by 45% simply by removing fluids.

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Table I. Analyses Used in Vessel Solids Investigation	
Analysis	**Methods Used**
Gross physical examination	Visual Observation, Photography
Microscopic Examination	Optical Microscopy, Photomicrography, Scanning Electron Microscopy
Particle Size Characterization	Sieve Analysis, Laser Interferometry, Scanning Electron Microscopy
Surface Chemistry	Scanning Electron Microscopy Energy Dispersive X-Ray Fluorescence, Electron Backscatter Imaging
Bulk Chemistry	Wavelength Dispersive X-Ray Fluorescence, Inductively Coupled Atomic Emission Spectroscopy
Mineralogy	X-Ray Diffractometry
Oil, Water, Solids Content	Gravimetric Thermal Retorting
Radiochemistry	HPGe Gamma Spectrometry

Table II. Oil, Water, and Solids Content, Mineralogy, and Particle Size Distribution for Vessel Solids

Sample	Oil	Water	Solids	Mineralogy from X-Ray Diffraction	Weight % of Particles > 180 μm	Size distribution for particles < 180 μm		
	Weight %					Q1	Median	Q3
11374-2	2.61	4.71	92.68	quartz, barite	57.72	5.66	16.76	29.00
11374-3	4.40	15.08	80.52	quartz, barite, ferroan dolomite, calcite	29.02	6.05	13.45	22.46
11374-4	1.19	5.13	93.68	quartz, barite (Sr substituted)	3.08	1.90	12.05	5.71
11374-5	7.75	7.75	84.50	quartz, barite, albite, bassinite	18.82	10.39	26.78	44.85
11374-7	nd	nd	nd	quartz, calcite	1.34	3.11	14.13	17.81
11374-8	2.20	11.63	86.17	quartz, barite	30.76	2.03	11.15	8.42
11374-9	6.77	10.04	83.19	quartz, barite	3.70	4.95	14.89	28.70
11374-10	11.96	28.13	59.91	quartz, barite, calcite, celestite	6.23	29.51	16.73	13.90
11374-11	1.17	0.75	98.08	barite, quarrtz	32.50	7.60	19.79	30.58
11374-12	0.65	15.56	83.79	quartz, barite	22.72	9.93	28.98	57.44
11374-57	9.72	15.14	75.14	quartz, barite, calcite, pyrite	7.72	4.66	15.68	48.74
11374-58	3.58	20.58	75.84	quartz	36.51	2.33	34.19	7.78
11374-80	1.55	24.37	74.08	quartz, barite, calcium rich albite	12.42	31.68	58.16	82.04
11374-81	5.99	10.75	83.26	quartz, barite, calcium rich albite	11.62	12.81	34.49	65.65
11374-82	1.82	15.87	82.31	quartz, calcium rich albite	23.30	32.75	69.88	106.22
11374-83	1.54	1.55	96.91	barite	85.08	8.13	25.91	69.10
11374-84	25.47	68.42	6.11	quartz, barite, calcium rich albite	1.36	9.61	32.36	32.12
Mean	5.52	15.97	78.51		22.58	10.77	26.20	39.44
Maximum	25.47	68.42	98.08		85.08	32.75	69.88	106.22
Q3	7.02	17.05	87.80		30.76	10.39	32.36	57.44
Median	3.10	13.36	83.23		18.82	7.60	19.79	30.58
Q1	1.55	7.10	75.67		6.23	4.66	14.89	17.81
Minimum	0.65	0.75	6.11		1.34	1.90	11.15	5.71

Table III. Major Constituents of Vessel Solids

Sample	SiO_2	$BaSO_4$ + $SrSO_4$	Al_2O_3	CaO	MgO	Na_2O	K_2O	TiO2	Cr_2O_3	P_2O_5	MnO	Fe_2O_3	FeO	LOI	Total
(weight %)															
11374-2	22.30	40.32	0.21	0.13	<0.01	0.30	0.28	0.263	<0.01	0.02	0.02	0.17	0.10	1.77	65.90
11374-3	14.20	31.87	1.21	1.72	0.06	0.60	0.28	0.344	0.02	0.07	0.22	28.10	18.70	4.93	102.32
11374-4	2.07	45.34	0.36	0.92	<0.01	0.28	0.13	0.287	<0.01	0.05	0.11	13.70	1.90	2.70	67.87
11374-5	77.40	4.82	1.66	3.01	0.10	0.81	0.62	0.451	<0.01	0.05	0.05	2.78	1.10	5.65	98.51
11374-7	72.00	7.44	0.42	4.39	0.08	0.49	0.25	0.232	0.02	0.03	0.06	7.93	2.90	6.62	102.86
11374-8	87.00	3.30	0.43	0.61	0.17	0.52	0.26	0.426	<0.01	0.05	0.02	1.50	1.10	3.85	99.25
11374-9	82.80	1.08	3.85	2.93	0.19	1.23	1.05	0.380	0.03	0.05	0.07	0.84	0.40	4.50	99.40
11374-10	24.20	28.55	2.66	2.88	0.35	0.67	0.44	0.351	<0.01	0.26	0.13	10.70	5.90	18.80	95.90
11374-11	1.99	46.41	0.32	0.12	<0.01	<0.01	0.18	0.269	<0.01	0.02	0.04	2.44	0.90	1.23	53.95
11374-12	88.50	6.84	0.45	0.31	0.14	0.20	0.21	0.234	<0.01	0.03	0.01	0.40	0.20	1.45	98.98
11374-57	2.62	19.39	0.11	11.40	0.07	2.90	0.06	0.114	<0.01	0.50	0.48	3.66	2.60	7.70	51.61
11374-58	87.00	0.68	1.54	3.39	0.36	0.40	0.36	0.227	<0.01	0.05	0.03	1.59	0.80	7.54	103.98
11374-80	62.90	17.39	4.48	0.93	0.25	2.44	1.04	0.242	<0.01	0.04	0.03	0.75	0.30	2.70	93.50
11374-81	62.00	19.61	3.53	1.35	0.56	1.18	0.86	0.226	<0.01	0.04	0.03	0.83	0.50	2.16	92.89
11374-82	84.70	2.33	4.54	0.82	0.22	1.29	1.10	0.236	<0.01	0.05	0.03	1.24	0.60	2.08	99.25
11374-83	1.27	48.46	0.59	0.36	<0.01	0.56	0.04	0.262	<0.01	0.14	0.01	0.50	0.20	0.62	53.03
11374-84	24.70	3.14	3.12	1.01	1.31	7.22	0.67	0.269	<0.01	0.09	0.04	2.22	2.00	34.60	80.40
Mean	46.92	19.23	1.73	2.13	0.30	1.32	0.46	0.283	0.02	0.09	0.08	4.67	2.36	6.41	85.86
Maximum	88.50	48.46	4.54	11.40	1.31	7.22	1.10	0.451	0.03	0.50	0.48	28.10	18.70	34.60	103.98
Q3	82.80	31.87	3.12	2.93	0.35	1.25	0.67	0.344	0.03	0.07	0.07	3.66	2.00	6.62	99.33
Median	62.00	17.39	1.21	1.01	0.19	0.64	0.28	0.263	0.02	0.05	0.04	1.59	0.90	3.85	95.90
Q1	14.20	3.30	0.42	0.61	0.10	0.47	0.21	0.234	0.03	0.04	0.03	0.83	0.40	2.08	66.88
Minimum	1.27	0.68	0.11	0.12	0.06	0.20	0.04	0.114	0.02	0.02	0.01	0.17	0.10	0.62	51.61

NOTES: Analysis on bulk sample basis; values lower than the detection limit for the analysis are indicated by <, for example <0.01

Table IV. Minor Constituents of Vessel Solids

Sample	Rb	Co	Ni	Cu	Zn	Ga	As	Se	Y	Zr	Nb	Mo	Sn	Sb	Ta	W	Tl	Pb	Bi
	ppm																		
11374-2	12	12	31	295	103	<3	6	6	<2	<3	<2	5	<5	41	3	79	9	145	22
11374-3	11	45	146	528	3750	<3	50	10	<2	<3	<2	49	<5	27	<2	107	14	572	9
11374-4	11	20	216	591	1170	<3	41	<3	<2	<3	<2	43	<5	64	36	<5	<5	1080	<3
11374-5	16	47	25	105	1670	10	64	22	<2	696	12	<2	<5	15	4	302	<5	531	7
11374-7	<2	38	71	754	108	<3	11	54	<2	80	5	30	141	47	<2	768	<5	76	6
11374-8	5	78	35	64	2700	14	540	42	<2	156	20	16	<5	25	25	597	<5	4500	7
11374-9	31	77	17	28	247	16	25	43	<2	578	11	<2	9	23	14	603	6	160	10
11374-10	7	34	115	713	10900	<3	234	7	<2	<3	<2	54	<5	73	<2	77	57	3950	<3
11374-11	<2	18	25	292	520	<3	6	<3	<2	<3	<2	53	<5	39	38	64	8	193	15
11374-12	<2	70	15	15	421	<3	37	40	<2	<3	7	<2	<5	<3	19	537	<5	306	<3
11374-57	8	31	90	353	21900	12	430	<3	<2	<3	<2	31	<5	<3	<2	<5	75	12300	11
11374-58	12	70	19	18	2310	<3	35	15	<2	276	9	<2	<5	17	12	578	<5	236	<3
11374-80	28	34	11	72	115	<3	67	8	<2	<3	4	<2	<5	36	17	259	<5	872	6
11374-81	25	35	29	731	271	<3	253	14	<2	<3	<2	<2	<5	30	14	494	<5	3480	<3
11374-82	32	86	32	91	204	<3	125	18	<2	213	7	<2	8	13	12	661	<5	919	<3
11374-83	14	15	52	404	291	<3	444	<3	<2	<3	<2	14	<5	48	79	55	<5	16200	26
11374-84	<2	28	56	82	11800	<3	192	10	<2	17	6	2	<5	3	<2	117	38	2150	<3
Mean	16	43	58	302	3440	13	151	22	<2	288	9	30	53	33	23	353	30	2804	12
Maximum	32	86	216	754	21900	16	540	54	<2	696	20	54	141	73	79	768	75	16200	26
Q3	25	70	71	528	2700	15	234	40	<2	427	11	48	75	44	28	588	48	3480	14
Median	12	35	32	292	520	13	64	15	<2	213	7	31	9	30	16	302	14	872	10
Q1	11	28	25	72	247	12	35	10	<2	118	6	15	9	20	12	93	9	236	7
Minimum	5	12	11	15	103	10	6	6	<2	17	4	2	8	3	3	55	6	76	6

NOTES: Analysis on bulk sample basis; values lower than the detection limit for the analysis are indicated by <, for example <0.01

Table V. Barium, Strontium, Barium:Strontium Ratio, Actinide Elements, ^{226}Ra and ^{228}Ra in Vessel Solids

Sample	Ba	Sr	Ba/Sr	S	Th	U	^{226}Ra	+/- 1σ	^{228}Ra	+/- 1σ
	ppm	ppm	mole ratio	ppm	ppm	ppm	pCi/g	pCi/g	pCi/g	pCi/g
11374-2	228000	7490	19.42	103000	24	<2	2142	107.0	1208	13.7
11374-3	182000	4470	25.98	76600	<2	<2	148	7.9	47	0.8
11374-4	231000	29000	5.08	105000	16	<2	152270	7619.0	29500	372.0
11374-5	26800	1270	13.46	14400	9	3	53	3.6	17	0.4
11374-7	40700	2470	10.51	21900	<2	2	1054	78.4	160	9.4
11374-8	18000	1140	10.07	11300	47	<2	29	2.1	11	0.3
11374-9	5730	513	7.13	4260	4	4	49	3.0	20	0.4
11374-10	162000	4820	21.44	80600	46	<2	667	34.0	105	1.9
11374-11	260000	10600	15.65	116000	<2	<2	2648	134.0	560	7.0
11374-12	39100	907	27.51	17100	8	<2	386	51.1	63	7.9
11374-57	106000	6560	10.31	151000	138	<2	7	0.9	2	0.2
11374-58	3520	382	5.88	6770	3	3	6352	350.0	1399	29.1
11374-80	101000	1070	60.23	43300	12	<2	36620	1856.0	12796	164.0
11374-81	110000	4380	16.02	48400	38	<2	117400	5883.0	49229	579.9
11374-82	12900	650	12.66	5530	13	<2	7772	453.1	3453	60.9
11374-83	247000	30900	5.10	121000	178	<2	723200	36540.0	49620	14440.0
11374-84	17800	535	21.23	63100	20	<2	6620	359.4	2556	42.0
Mean	105385	6303	16.92	58192	40	3	62201.0		8867.3	
Maximum	260000	30900	60.23	151000	178	4	723200.0		49620.0	
Q3	182000	6560	21.23	103000	44	3	7772.0		3453.0	
Median	101000	2470	13.46	48400	18	3	2142.0		560.0	
Q1	18000	907	10.07	14400	10	3	148.0		46.5	
Minimum	3520	382	5.08	4260	3	<2	7.1		1.5	

Figure 1. Relationship of ^{226}Ra activity to $BaSO_4 + SrSO_4$ content .

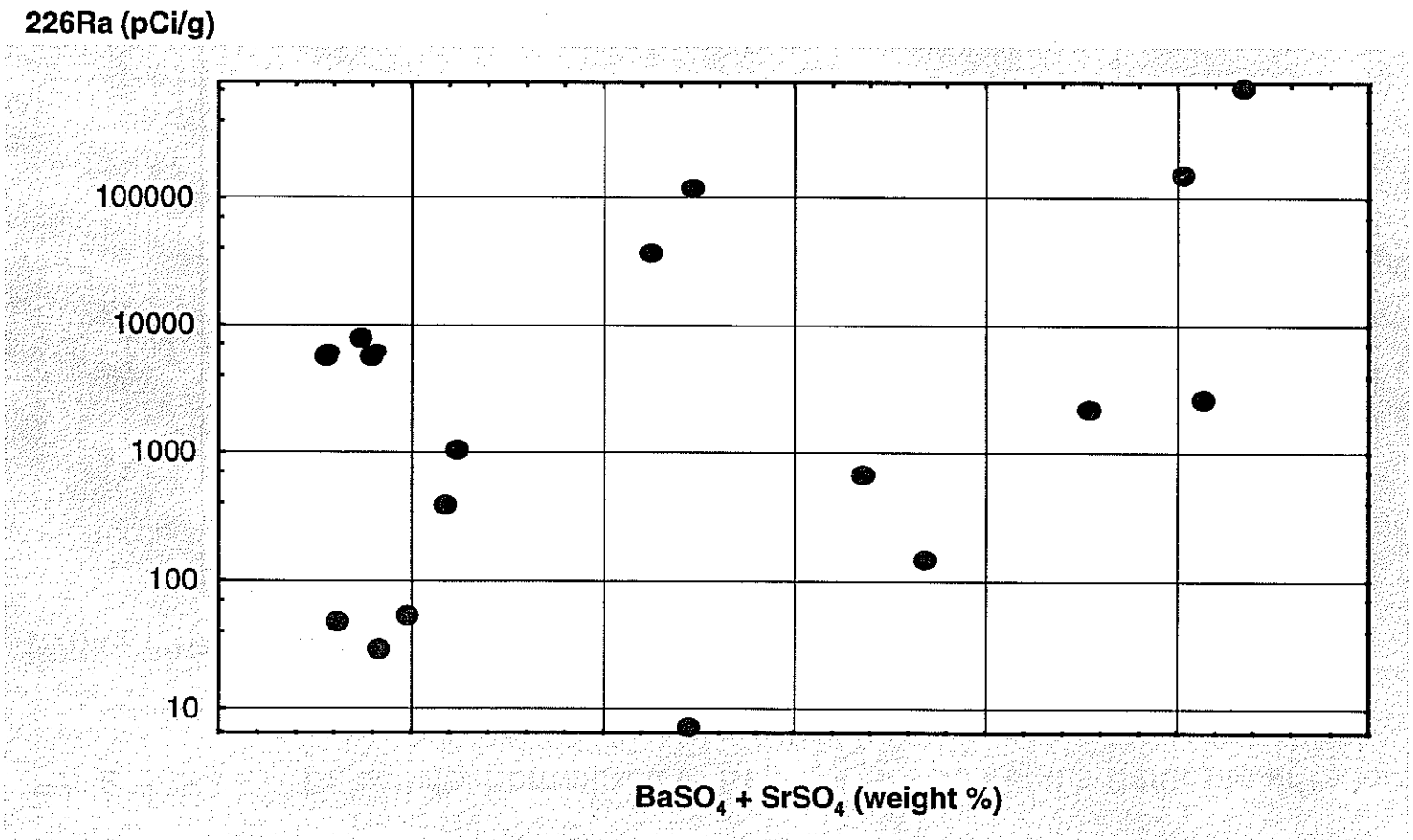


Fig. 2 $^{226}Ra + ^{228}Ra$ activity normalized to $BaSO_4 + SrSO_4$ versus Ba/Sr molar ratio.

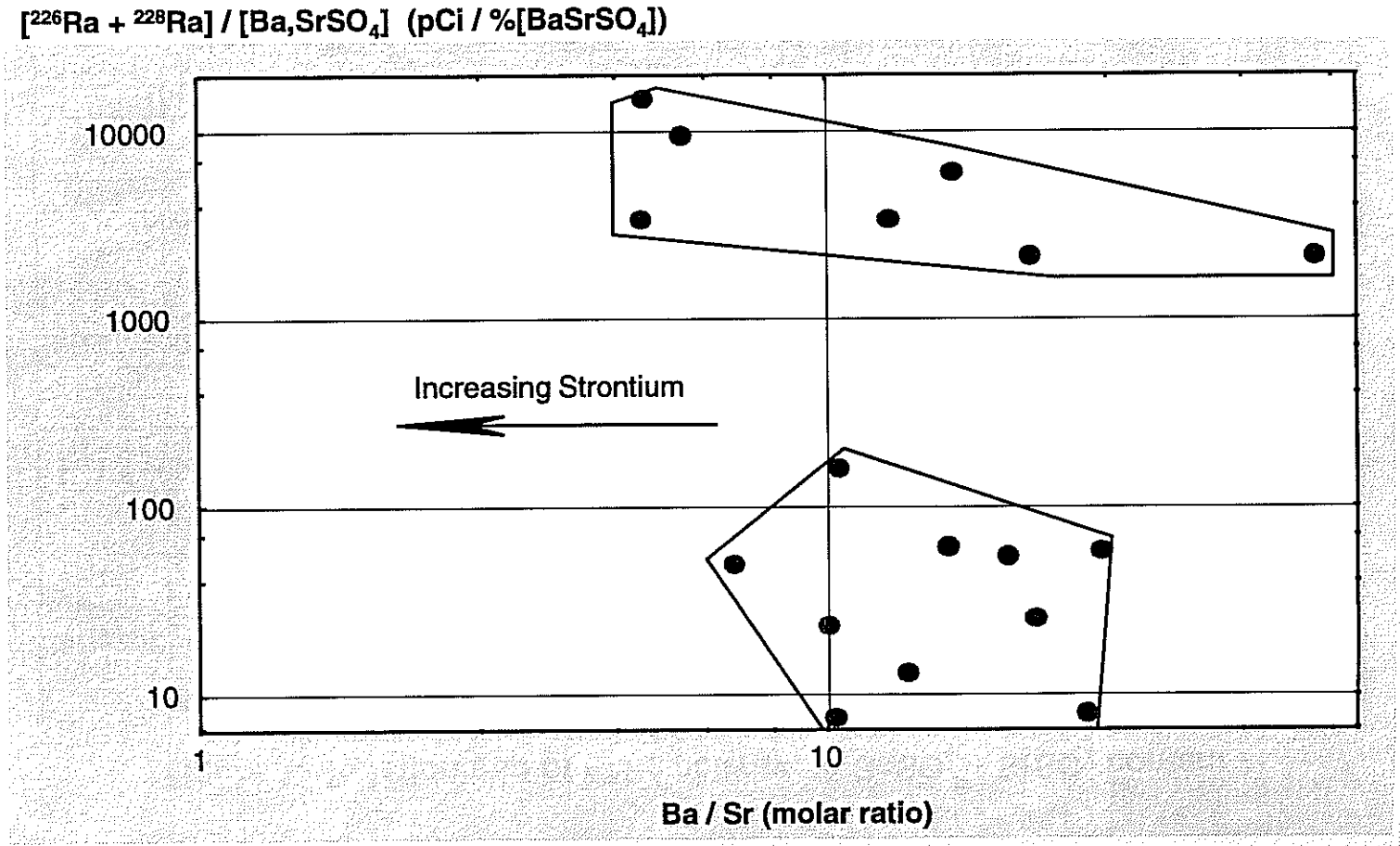
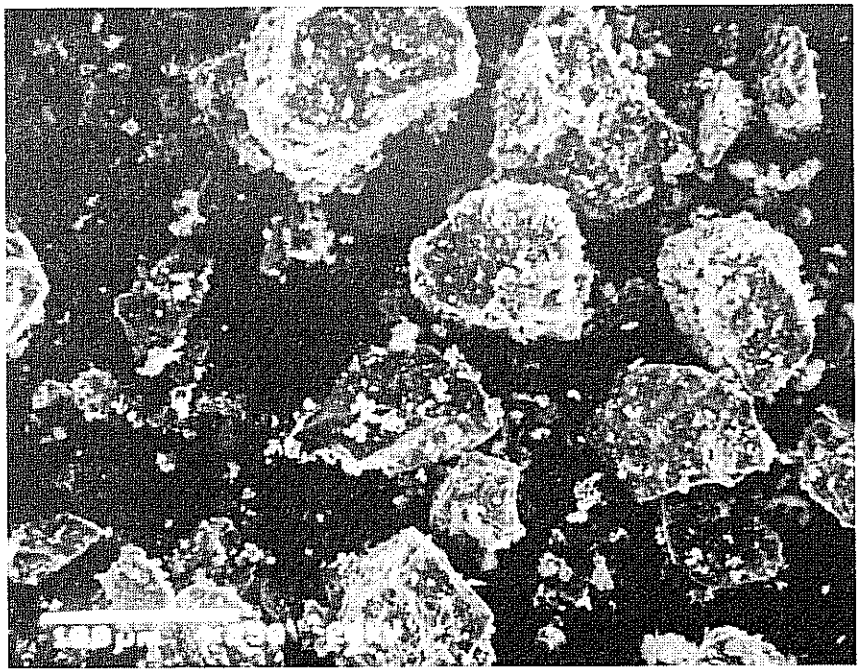


Figure 3. SEM photographs of barite-poor vessel solids (<180 μm fraction; sample 11374-9). (A) x150 image showing particle morphologies. (B) x500 image showing detailed particle morphologies. (C) x150 image showing barium X-ray map of image shown in (A). (D) x500 image showing barium X-ray map of image shown in (B).



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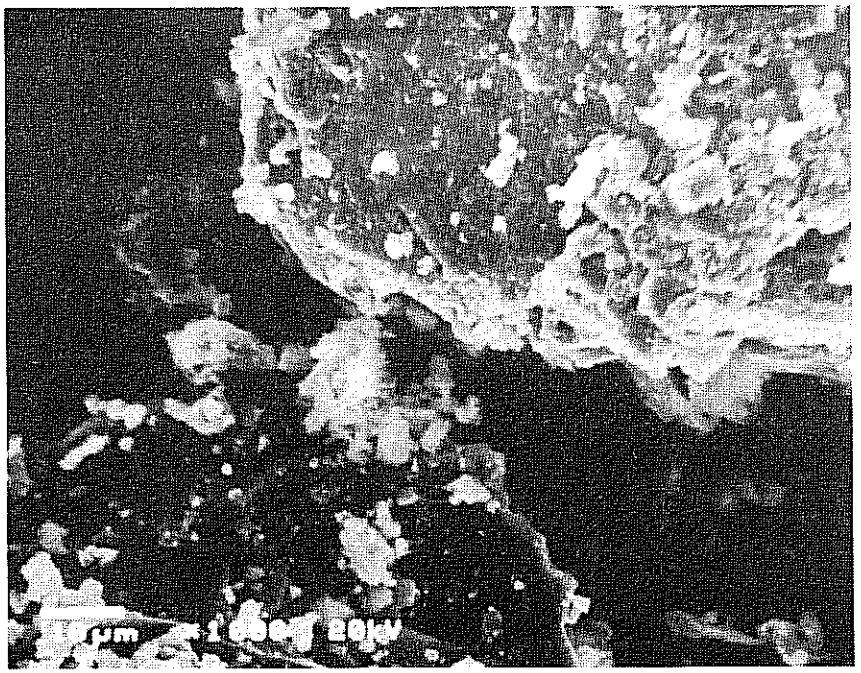

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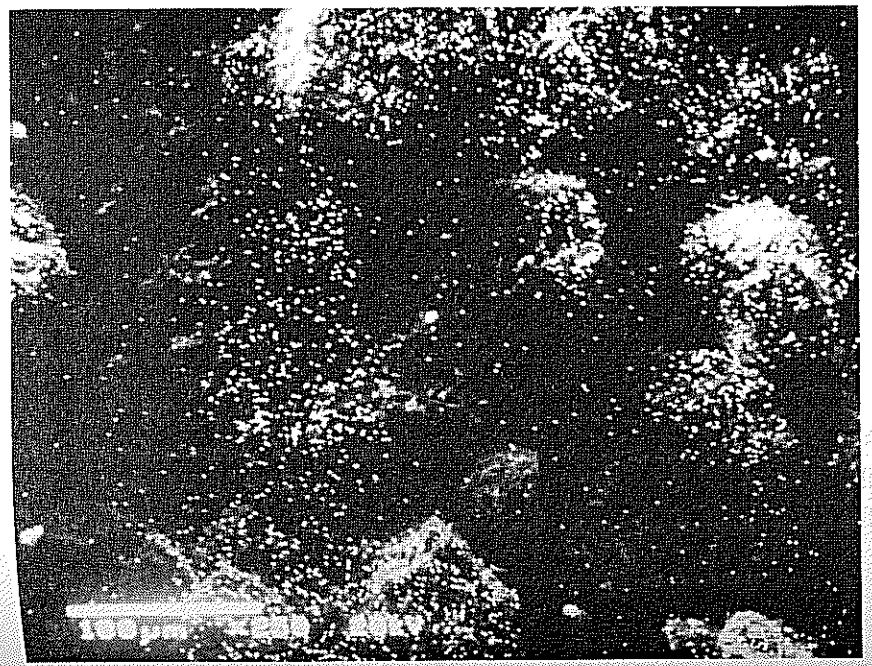

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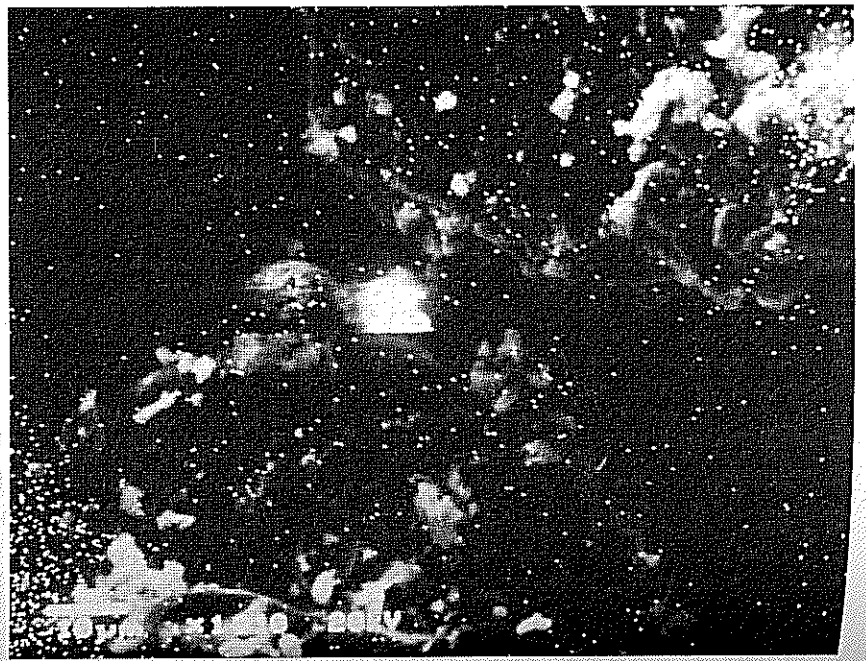
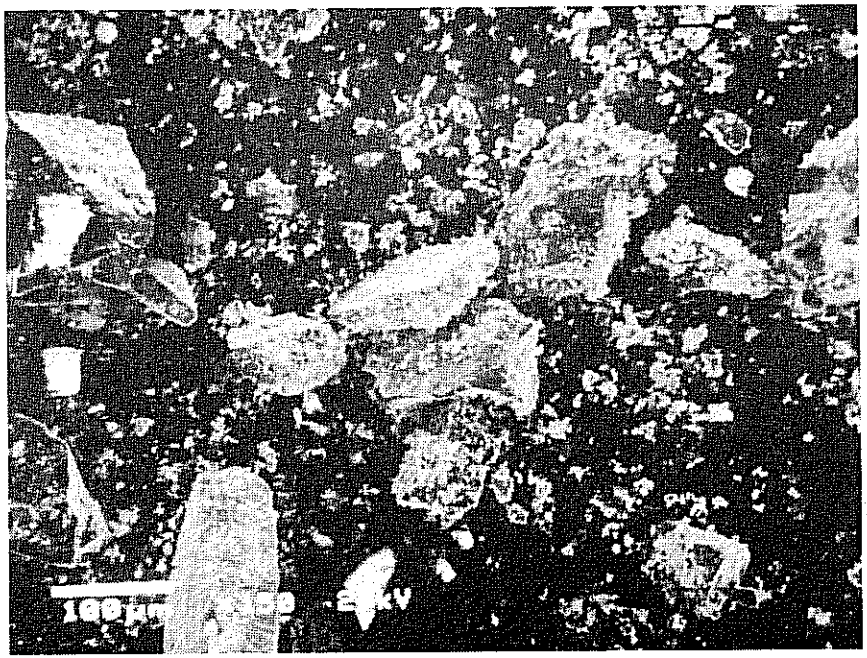


Figure 4. SEM photographs of barite-rich vessel solids (<180 μm fraction; sample 11374-2). (A) x150 image showing particle morphologies. (B) x500 image showing detailed particle morphologies. (C) x150 image showing barium X-ray map of image shown in (A). (D) x500 image showing barium X-ray map of image shown in (B).



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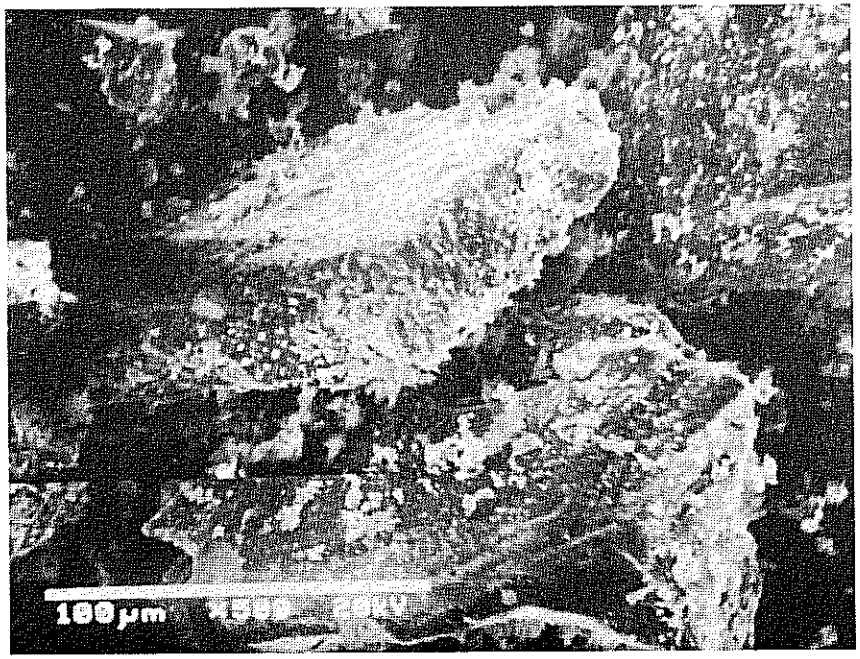

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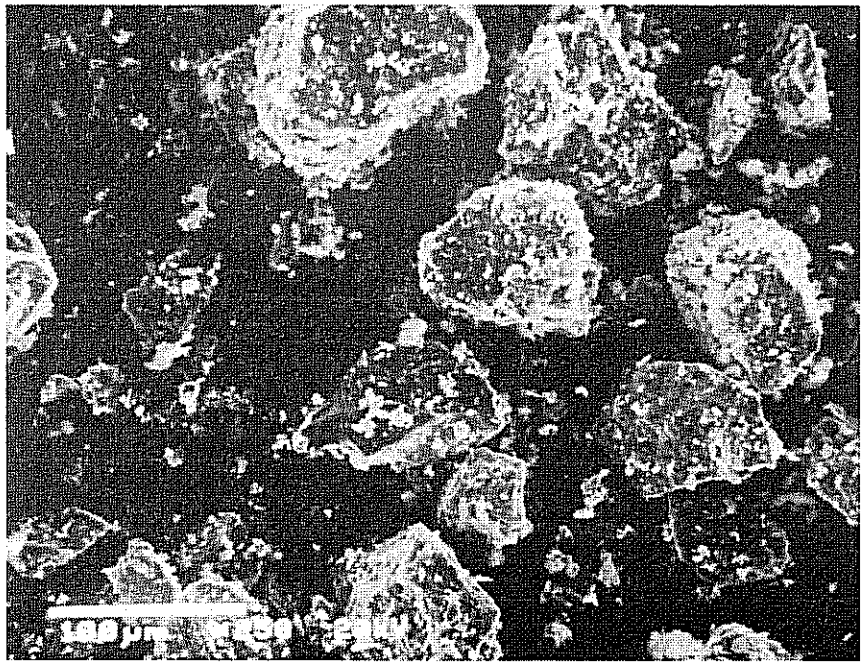
Figure 3. SEM Photographs of barite poor vessel solids (sample 11374-9). (A) x150 image showing particle morphologies. (B) x500 image showing detailed particle morphologies. (C) x150 image showing barium X-ray map of image shown in (A). (D) x500 image showing barium X -ray map of image shown in (B).



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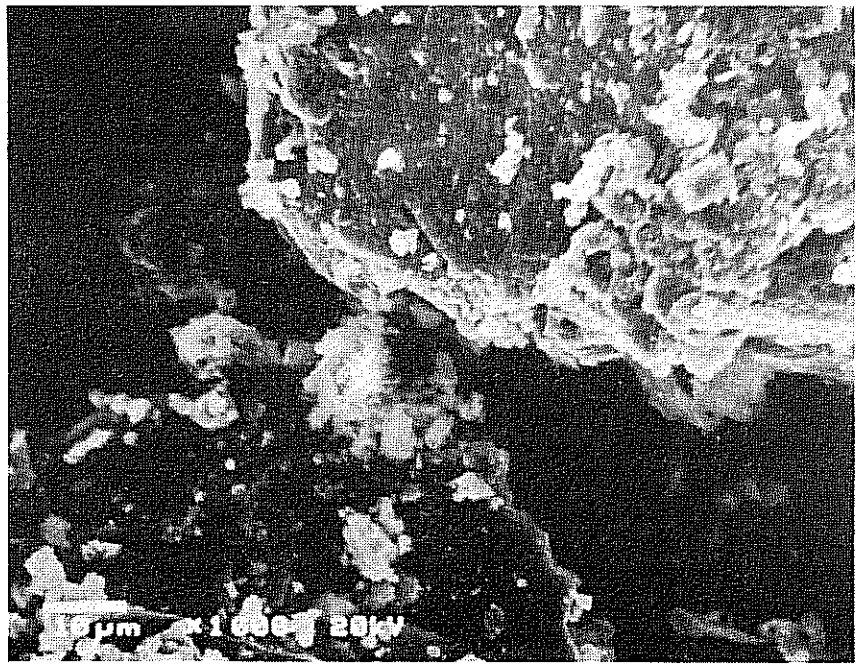

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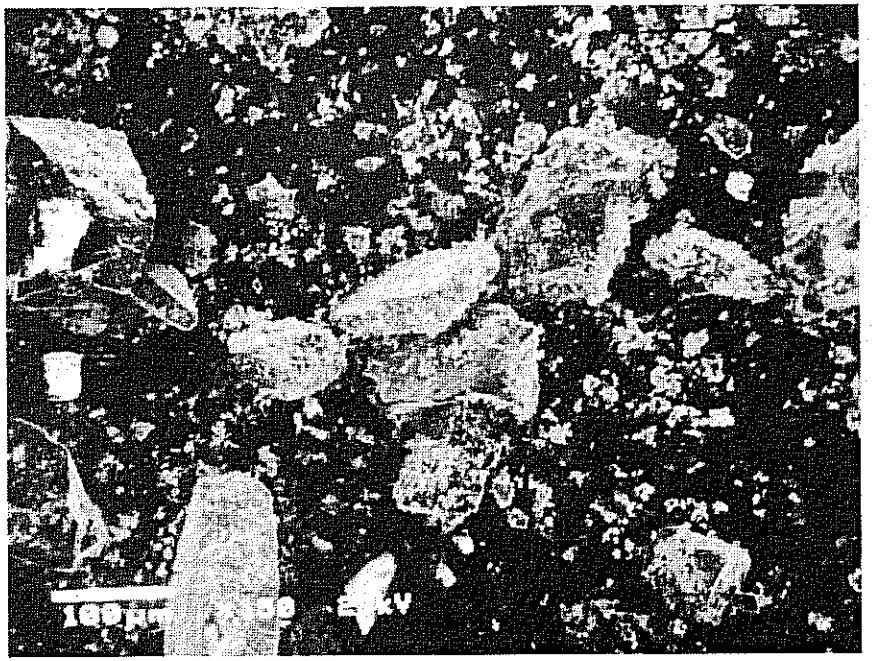
Figure 4. SEM Photographs of barite rich vessel solids (sample 11374-2). (A) x150 image showing particle morphologies. (B) x500 image showing detailed particle morphologies. (C) x150 image showing barium X-ray map of image shown in (A). (D) x500 image showing barium X -ray map of image shown in (B).



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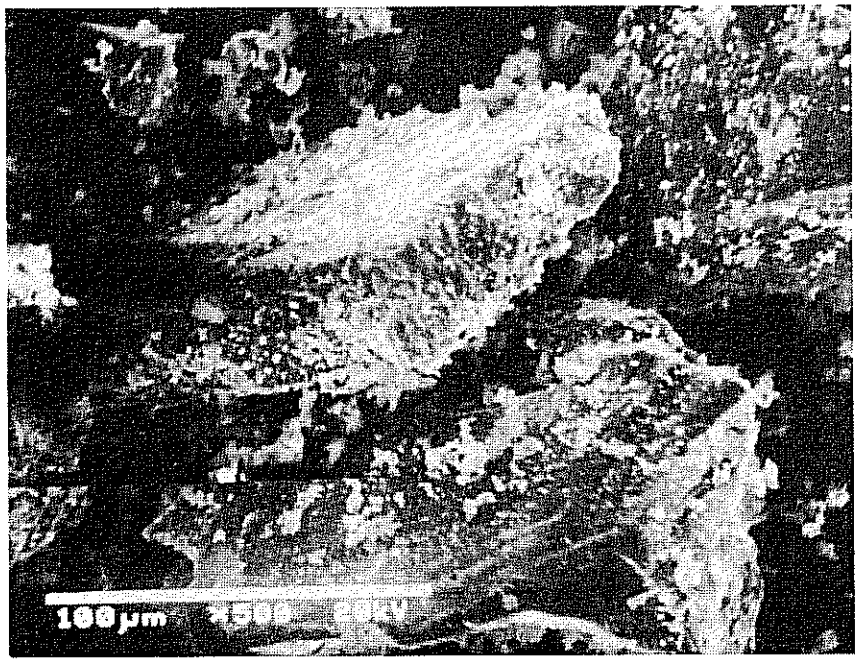

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Volume Reduction And

Decontamination Of Norm

Patricia Welther, P.E.
Phoenix Environmental Services, Inc.

Jim Burton
Source Environmental Services, Inc.

ABSTRACT

The identification of Naturally Occurring Radioactive Material (NORM) in oil and gas production equipment and sludges has placed an additional financial burden on the industry and heightened health and safety concerns for the workers. Source Environmental Services, Inc. has developed a system that can greatly reduce both the health concerns and the financial burden for the generators of NORM. The system is designed to process the NORM contaminated oil, water and solids to remove the NORM from the water, oil and bulk of solids which results in a small volume of NORM to be disposed of.

Most of the material that is drummed and identified as containing NORM contains a significant amount of water, oil and debris that can be decontaminated. This results in a substantial volume reduction. The high cost of disposing of NORM, as compared to Non-hazardous Oilfield Waste (NOW) and the deep well injection of water provides the economic justification for the volume reduction. Typically, a drum of NORM contains only 10 to 20 percent NORM contaminated solids with the rest being water and oil. The volume reduction process includes grinding and crushing the solids in order to expose more of the matrix to the cleaning process. This also produces, as a benefit, an additional volume reduction as the creushed and dewatered material fills fewer drums.

Because traditional tank cleaning operations generate a large volume of waste containing mostly water used in the cleaning process, Source teamed up with HBM Environmental (HBME) to utilize their "state of the art" patented Robotic Tank Cleaning System. HBME developed this fully robotic waste fluidization and removal system to provide a means of cleaning tanks within the new "limited confined space entry" regulations under OSHA. This system has been used in refineries, petroleum terminals, the petro-chemical industry, the paper industry, and in the oilfield to quickly and safely remove waste without the need to put personnel at risk of exposure to dangers encountered with tank entries. The Robotic System utilizes a recycle system to greatly minimize the amount of wash fluid which becomes contaminated with NORM. This

provides the team of Source and HBME with a means to integrate the volume reduction process and further reduce the material contaminated with NORM requiring high disposal costs.

When NORM contaminates soil, Source utilizes Tubescope VETCO's patented Soil Washing System to separate the NORM contaminated material from the soil. This system is very economical for processing large volumes of contaminated material that are typically found at pipe yards. The NORM processing expertise of Source combined with the diverse experience of Tubescope, offers the industry a cost effective means to process NORM in various forms.

This paper will review the many projects completed by Source that have provided the producers with significant savings in the disposal of the NORM contaminated solids, oil, and water. The decontamination and volume reduction process will be discussed in detail. The various options for disposal of the concentrated NORM as well as solids preparation required to utilize each option will be discussed.

REGULATIONS

NORM generators are required to obtain a General license under LAC 33: XV, Chap. 14 of the Louisiana Radiation Regulations. Anyone that operates a NORM waste reduction process or conducts decontamination activities is required, under the same regulations, to obtain a Specific license. Most states recognize the Specific license from Louisiana as valid to process in their state. Source has been operating under a Specific license since early 1993. Each time a project is to be conducted, the Louisiana Radiation Protection Division requires a work authorization be obtained prior to the start of activities. The Louisiana statutes require that any person handling or processing NORM is required to be licensed under the Specific license guidelines.

The health and safety concerns are addressed in the OSHA respiratory protection (29 CFR 1910.134), potential benzene exposure (29 CFR 1910.1028), and Hazard Communication (29 CFR 1910.1200) standards. Another guideline followed by Source and HBME is the API RP-2015, "Recommended Practice for Cleaning Petroleum Storage Tanks".

VOLUME REDUCTION OF NORM

The identification of NORM in oil and gas production equipment and sludges has placed an additional financial burden on the industry and heightened health and safety concerns for the workers. Source has developed a system that can greatly reduce both the health concerns and the financial burden for the generators of NORM. The system is designed to process the NORM contaminated oil, water and solids to remove the

NORM from the water, oil and bulk of solids which results in a small volume of NORM to be disposed of.

Because the NORM is often attached to oil sludges and fine solids, the volume reduction system is most effective by breaking the bond between the oil and NORM and then filtering the fine NORM contaminated solids from the wash water. The solids are washed to remove oil and the fine solids contaminated with radionuclides. The decontaminated water is disposed of, typically through down hole injection; the oil is returned to the producer for recycling; and the decontaminating NOW solids properly disposed of in a commercial facility. The concentrated NORM is stored in drums for disposal in an appropriate manner.

Most of the material that is drummed and identified as containing NORM contains a significant amount of water, oil and debris that can be decontaminated. This results in a substantial volume reduction. The high cost of disposing of NORM, as compared to NOW and the deep well injection of water provides the economic justification for the volume reduction. Typically, a drum of NORM contains only 10 to 20 percent NORM contaminated solids with the rest being water and oil. The volume reduction process includes grinding and crushing the solids to be able to reach all the surfaces that could contain the NORM. This also produces, as a benefit, an additional volume reduction as the crushed and dewatered material fills fewer drums.

Typically, for each 100 drums of NORM processed, only 13 drums of NORM would require disposal; 4 drums of NOW is produced; and 83 drums of decontaminated water and oil is separated and disposed of and/or recycled.

PROCESS DESCRIPTION

The process of NORM waste volume reduction varies depending on the volume and composition of material that is contaminated. For the typical NORM contaminated tank bottoms in the oilfield, petroleum terminal or refinery, the first phase in the process is the removal of the contaminated tank bottoms. This is the most critical step in the waste minimizing process. The goal is to minimize the generation of NORM contaminated wash water in order to minimize the overall volume of NORM removed from the tanks. This unique system employed by HBME has demonstrated that the contaminated tank bottoms can be removed and the tank cleaned with only a minimal increase in the volume requiring NORM processing. The patented fully robotic fluidization and recycle system can clean a typical tank in record time and with minimal worker exposure because the Robot is the only one that enters the tank. Figure 1 and Figure 2 illustrate two alternative ways to remove NORM contaminated tank bottoms. When using this system of sludge removal, the recovered and separated NORM solids are pumped directly into the solids washing unit of the Source process.

When the NORM has been stored in drums, the drums of contaminated material are loaded into a decontamination booth where an operator wearing appropriate protective equipment opens the drums and empties the contents into the sump. The operator uses water spray nozzles to flush the material from the drums. The material flows over the first of several screens which allow the operator to remove large debris and metal prior to processing in the sump. A chopper pump located in the sump breaks up large particles in order to be able to adequately wash all the oil and NORM from the solids.

The slurry is pumped through a blender to further reduce the particle size and wash the solids. As the slurry flows over the second screen, an operator assisted with ban magnets removes large debris and metal from the solids as they flow into the sludge feed hopper. The liquids that flow through the screen are recycled to the sump to slurry additional solids. Excess liquids are treated to required standards prior to disposal.

Solids Washing

The solids from the sludge feed hopper are discharged into the first of three solids washing tanks where agitation, chemicals and enzymes wash the solids of oil and NORM. Induced air flotation lifts the recovered oil and NORM contaminated fine solids to the surface where they are skimmed into the waste water treatment system. The tanks are insulated and can be heated, if required, to break tight emulsions. The inclined dewatering screws transfer the coarse solids from the first tank to the second and then to the third. After the third washing, the solids are dewatered in the inclined screw and discharged onto the third shaker screen.

The dual screen vibrating shaker separates the liquid to be processed and recycled from the solids. In most situations, the larger solids have been decontaminated sufficiently to meet the criteria set for NOW. The finer solids which are recovered in the lower screen may be NOW or NORM, depending on the characteristics of the original solids processed. Because of the high level of oil and water that typically exists in the drums contaminated with NORM, the volume reduction process results in only a fraction of the number of drums of solids when compared to the number of drums processed.

Waste Water Recycled

The waste water is treated to recover the oil and remove the fine solids. These fine solids, which are typically classified as NORM, are tested and disposed of in the appropriate manner. The water is recycled in the wash unit to minimize the chemical and enzyme use and limit the amount of water that requires disposal. The waste water treatment system includes the use of gravity separation, centrifugation and filtration down to 5 microns.

CASE HISTORY

Source recently completed a volume reduction project in Morgan City, Louisiana for a Major Oil Company (1). The Company employed a third party to remove tank bottoms from oil storage tanks and to supply drums of material and bulk liquids for processing. The storm water from the project was collected and also processed in the volume reduction unit to eliminate the potential for a release of NORM into the environment.

Project Definition

The Company had generated a total of 388 drums of NORM, an estimated 819 drums of barge water and an estimated 1,229 drums of storm water from the process area. As Figure 3 illustrates, a total of 75 drums of NORM, 21 drums of NOW, and 2340 drums of oil and water were recovered from the volume reduction process. With the low solids content of the barge and storm water, the volume reduction exceeded 99 percent for this material. The volume reduction from the solids processing was 86 percent. Of the solids generated, 22 percent were washed and decontaminated of the NORM so they met the standards to be classified as NOW, significantly reducing the disposal cost.

Cost Summary

The cost of transportation and disposal of the NORM is excessive and can exceed $1,000.00 per drum. The volume reduction system is cost effective because of the substantial decrease in NORM that is achieved. Source is also developing an encapsulation system that will reduce the cost of NORM disposal substantially, providing even greater savings for the generators. Table 1 summarizes the cost benefit analysis of the Morgan City project. The cost of disposal of NORM contaminated water assumes only the contaminated barge water and not the storm water from the process area. Even when the NORM is only being collected and drummed, storm water must be collected and treated but this water does not typically contain high levels of radionuclides.

The generator saved almost $1,000,000 in disposal costs by employing the volume reduction technology to reduce the estimated volume of NORM from 1,207 drums to only 75 drums of NORM requiring disposal. As the encapsulation system is integrated into the volume reduction unit further savings will be realized.

SOIL WASHING

When the NORM contaminates large volumes of material as is typical of pipe yards and production facilities, the integrated soils washing system provided by Tubescope VETCO and Source can provide the client significant cost savings over alternative technologies. Many times when a generator determines that an area has contamination, the area is excavated and stored in drums until the generator can figure out what to do with the NORM. This process typically generates an excessive amount of contaminated material. With the integrated soil washing and NORM processing system, the areas can

be remediated on-site with the decontaminated soils returned to the excavation and the volume reduced NORM disposed of at an approved facility.

DISPOSAL OPTIONS

Disposal of NORM presents some formidable problems. Solutions are complex and typically involve a cross-section of technical and social issues. Currently there are few options for disposal of NORM. Two landfills, one in Utah and one in Washington, are permitted to accept NORM (2) provided the waste is proved non-hazardous according to USEPA Guidelines. Land application, as proposed by a permit application for a landfarm in Louisiana, is associated with a significant potential liability to the generator. Many in the industry are promoting returning the material back to the source through deep well injection or encapsulation during plug and abandonment of wells. Land application and downhole placement are associated with a significant cost and liability. Today many generators are just storing the waste in the hopes that the market will develop a less expensive alternative. Only time will tell if this wait and see strategy is an economical one.

CONCLUSION

Addressing NORM contamination requires pre-planning to minimize the volume of waste in the removal process. For tank bottoms, an integrated tank cleaning and NORM processing system provides cost effective volume reduction. NORM contaminated soils can be effectively remediated on-site using the patented soil washing system integrated with the NORM volume reduction system. These two systems provide the customer the most significant savings in removing and processing NORM. When the NORM has already been stored n drums, the volume reduction process can produce significant savings.

REFERENCES

1. Welther, P. and Burton, J., "Significant Savings Realized Through Volume Reduction of NORM," in proceeding at the Petro-Safe '94 Conference. Houston, Texas. Pennwell Conference, 1994.

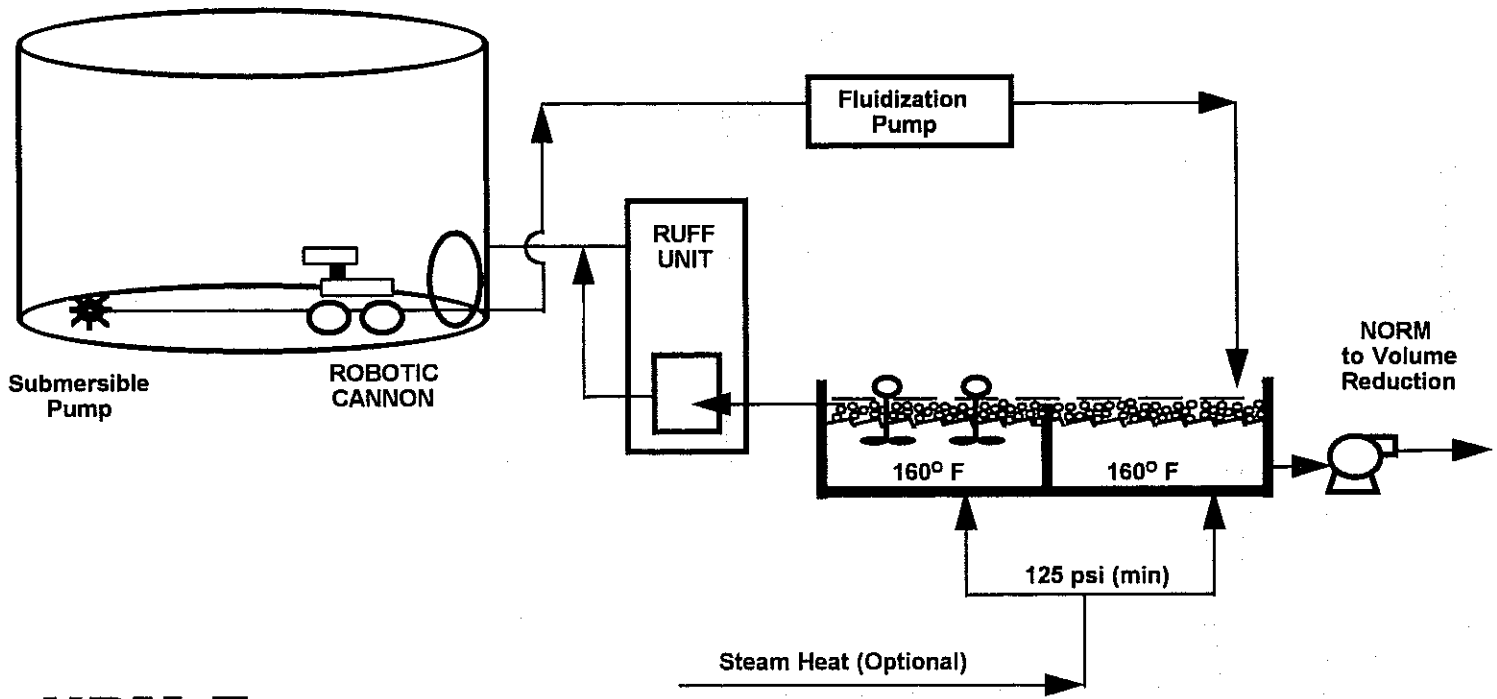
2. Wilson, W.F., "NORM Disposal Options," in proceeding of the Petro-Safe '94 Conference. Houston, Texas. Pennwell Conference, 1994.

TABLE 2

COST BENEFIT ANALYSIS

CASE	ITEM	UNIT COST	TOTAL COST
Total Transportation & Disposal NORM w/o Processing	**1,207 bbls**	**$1,000**	**$1,207,000**
Processing Service Cost	2,436 bbls	$ 79	$ 192,000
Trans. & Disposal of Recovered Water & Oil	2,340 bbls	$ 1	$ 2,340
Trans. & Disposal of NOW (Drums)	21 bbls	$ 8	$ 168
Trans. & Disposal of NORM (Drums)	75 bbls	$1,000	$ 75,000
Total Cost With Processing	**12,436 bbls**	**$ 111**	**$269,508**
TOTAL SAVINGS FROM PROCESSING	**1,207 BBLS**	**$777**	**$937,492**

Figure 1
Fully Robotic NORM Removal

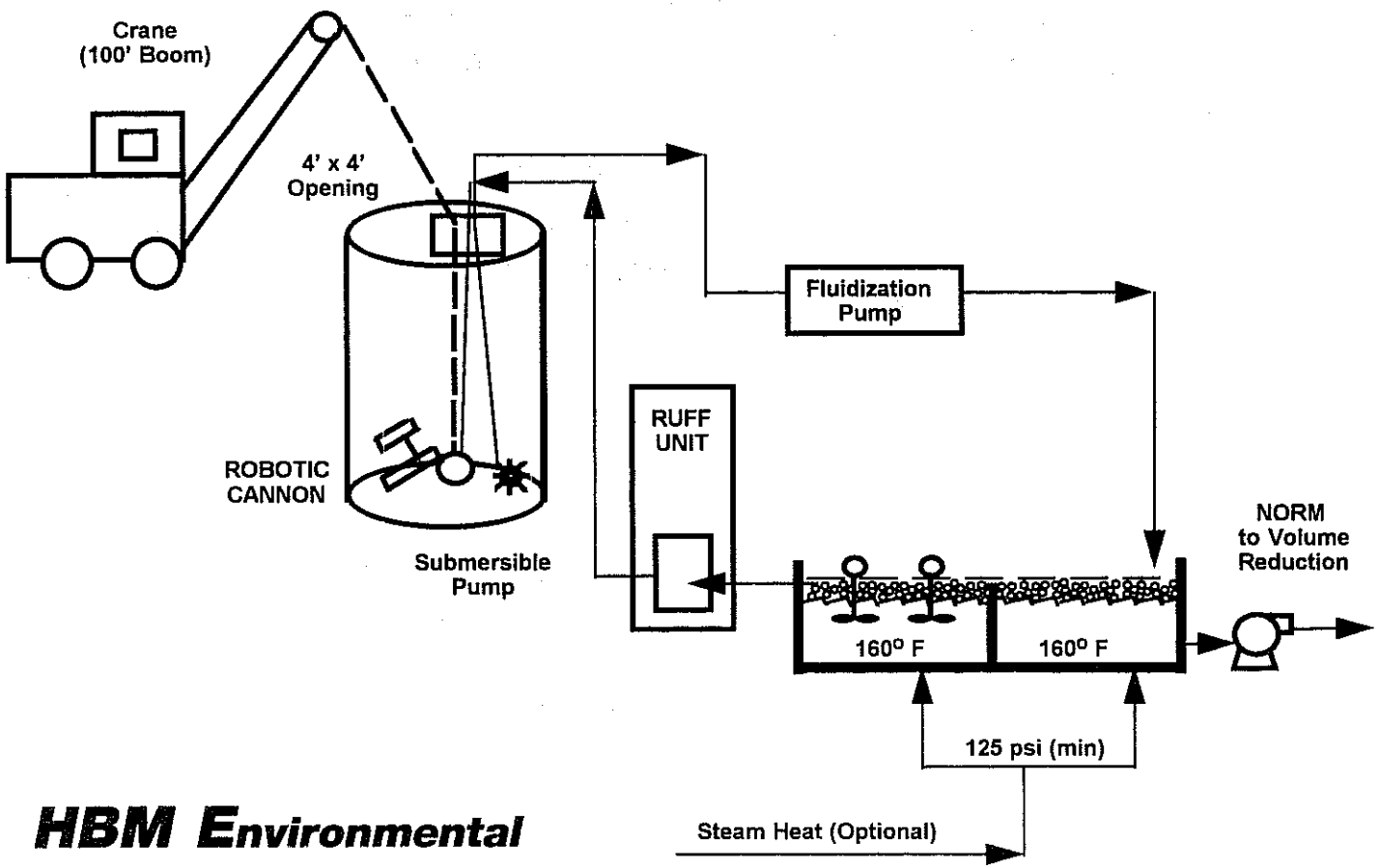


HBM Environmental

Figure 2

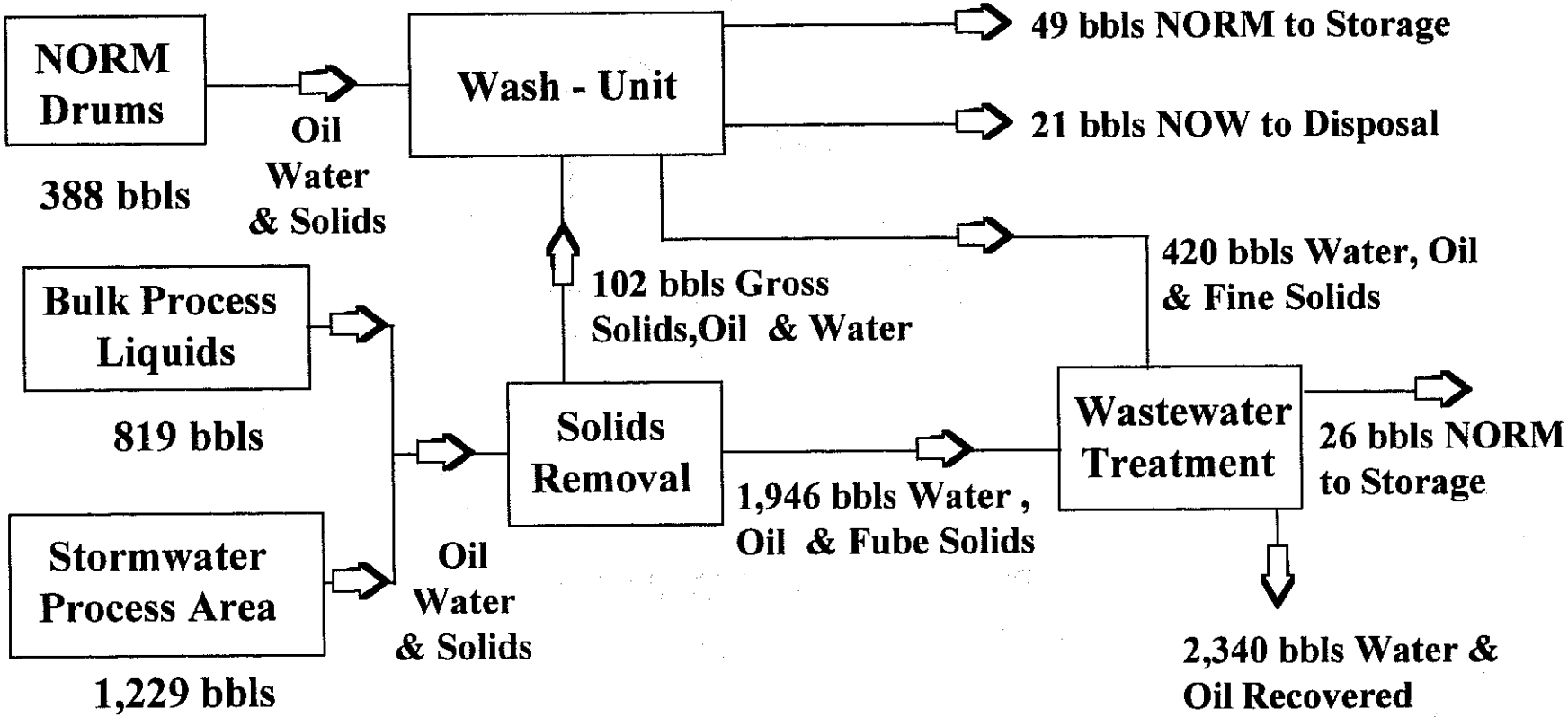
Robotic NORM Solids Removal

Optional Top Tank Entry for High Sludge Levels



HBM Environmental

Figure 3
NORM Volume Reduction System
Mass Balance



Source Environmental Services, Inc.

Downhole Disposal of NORM Wastes in an Offshore Setting: Lessons Learned

William W. Scaife
Steven G. Mueller
and
Danny R. Young
Amoco Production Company

ABSTRACT

Increasing regulatory restrictions on naturally occurring radioactive material (NORM) associated with oil and gas production are requiring the oil and gas industry to develop innovative disposal procedures in the offshore environment.

The Offshore Business Unit of Amoco Production Company has completed two NORM disposal projects in conjunction with plug and abandonment operation on wells in Offshore Continental Shelf waters. In July of 1992, 36 drums of NORM contaminated scale, sands and solid materials were slurried and placed as a balanced plug in an offshore well in the West Delta area. Material that could not be slurried was encapsulated in casing and disposed of in the same well. In May of 1993, 31 drums of NORM contaminated materials were encapsulated in casing and placed in an abandoned well in the South Timbalier area. Both projects were designed to ensure the safety of personnel involved, while achieving the main objective of permanently disposing of the NORM contaminated material.

Post evaluation of the Amoco West Delta project identified four areas for potential improvement:

- Drumming and cleaning procedures
- Equipment design
- Slurry procedures
- Personnel safety and monitoring

Lessons learned during the West Delta project were successfully incorporated into the planning and execution of the South Timbalier project.

INTRODUCTION

Amoco Production Company operates six oil and gas producing fields in the Gulf of Mexico Offshore Continental Shelf waters where naturally occurring radioactive material (NORM) is being produced along with the oil, gas and produced water. NORM has been found associated with sands and sludge removed from production vessels and scale deposited on the walls of tubing, flanges, separators and other equipment.

Amoco has disposed of NORM contaminated materials during two plug and abandonment operations in wells on the Gulf of Mexico Offshore Continental Shelf. Both projects were permitted through the Minerals Management Service and carried out by personnel trained in the handling of NORM. Downhole disposal was chosen because it is viewed as a permanent disposal method with a high degree of isolation, which minimizes future liability.

WEST DELTA DISPOSAL PROJECT

The West Delta Block disposal project took place in July of 1992 and involved 36 drums of NORM contaminated material. Substantial variation was encountered in the material disposed of during the project. Liquids ranged from wash water to oil-water-paraffin mixtures removed from production vessels. Solids included scale removed from tubing, produced sands from separators and miscellaneous refuse found in the drums. Refuse included plastic buckets, oilmops, filters, pneumatic tubing, and steel bolts.

Planning - The project was permitted through the Minerals Management Service to have two distinct operational phases. Phase 1 was a procedure to slurry the material and then pump the slurry downhole. The slurry was left in a balanced position in the tubing and production casing annulus. Phase 2 involved placing the material that could not be ground and slurried inside a sealed casing string, lowering the string into the surface casing and then completing the abandonment procedure.

Primary and secondary wells were selected for the project. The secondary well would serve as a backup in the event problems were encountered when pumping down the primary well. The wells were selected for the following reasons: 1) both wells had sufficient volume to hold the entire

slurry plus cleanup water, 2) both were single completions with no mechanical impairments, 3) both lacked surface pressure and 4) the wells were relatively new without much drilling wear or corrosion in the casing.

Equipment and personnel were supplied by a contractor. Primary criteria for selection of contractors were personnel training and equipment capability. All personnel handling the NORM contaminated material were required to have specialized NORM training. Both the contractor and Amoco had trained Radiation Safety Officers (RSOs) on site to monitor personnel.

Equipment for the project included a slurry tank, a grinder, triplex pumps, and associated hoses. The equipment was inspected and evaluated prior to letting the contract.

The original plan was to make 2 slurries. The first slurry would contain the scale, produced sand and separator bottoms. The second slurry would contain the refuse material that could be ground. Pumping two slurries would keep the volume to a manageable amount and the fluid weight could be more easily controlled. After pumping the two slurries, the equipment would be decontaminated and the rinsate would be pumped downhole in a final pumping.

Implementation - On the first day the 36 drums were opened, sorted and mixed into a 47 barrel slurry. Grindable materials were set aside. Items that could not be ground were put into drums prior to being placed in sealed casing capsules. The pumping operations were begun in mid afternoon. After 25 bbls of the slurry was pumped down the primary well, equipment failure forced the shutdown of the operation for the night.

The following day the decision was made to pump the remaining material down the backup well. The decision to use the backup well was based on concerns that in the intervening time, the primary well might be plugged due to the settling of the material out of the slurry. The remaining material was pumped down with no further problems encountered. The contractor equipment was decontaminated and the rinse water was pumped down the backup well.

Phase 2 dealt with the materials that could not be ground up. Eight joints of 7 5/8" casing had been prepared onshore. The first joint had a plate welded onto the end to form the bottom of the capsule. The last joint had a plate welded on it to seal the top of the capsule. A "J" latch was fabricated to be used to used to lower the casing string into the wellbore.

The well was prepared to receive the capsule by pulling 500' of the 7" production casing. The first casing joint was suspended in the wellbore. The NORM material was then removed from the drums and placed into the 7 5/8" casing. The next joint was made up, run into the hole and the process was repeated. Six joints were used to encapsulate the remaining NORM contaminated material.

The area was decontaminated, surveyed, and the 7 5/8" casing was sealed by the combination coupling/ "J" latch. The 120' of casing was lowered inside the 10 3/4" surface casing and placed on top of the 7" casing still in the wellbore. A cast iron bridgeplug (CIBP) was set on top of the capsule and a cement plug was spotted over the CIBP.

Post evaluation - Four areas for improvement were noted during the operation.
1) Drumming and cleaning procedures
2) Equipment design
3) Slurry procedures
4.) Personnel safety and monitoring

Drumming and cleaning procedures - Drumming and cleaning procedures could be improved by ensuring thorough separation of the NORM sands, scales and sludge from extraneous materials such as filters, nuts and bolts. As much separation as possible should be done prior to project initiation. Excessive time was spent sorting and decontaminating material that was mixed in with the drums of scale and sand. Extreme care should be taken to ensure that small pieces of tubing, broken plastic and other refuse does not end up in the slurry material. This type of foreign material affected equipment operations, particularly the triplex pumps used to pump the material downhole.

Employees and contractors must make a concerted effort to place only NORM contaminated materials into the drums. The variety of materials found in the drums indicated that in addition to NORM, other materials were being disposed of in the drums. Additional time had to be spent sorting and decontaminating this type of materials. Waste volume and project time could have been minimized by only having to deal with sands, sludge and scale.

Equipment design - Equipment must be designed specifically to handle the material that will be encountered. Grinders should be able to grind plastics, filters, and tyvex suits. Ideally the grinder should be able to deal with metals and harder material that are missed during the sorting process.

Equipment should incorporate appropriate containment measures for operation in the offshore environment. Slurry tanks should have drip pans underneath. Hoses, manifolds and pumps should also be on drip pans or have similar containment features. Drum cleaning and material sorting areas should have adequate means of preventing splash over. Planning in this area will minimize the decontamination effort.

Slurry operations - Consideration should be given to doing the slurry operations onshore. Onshore slurrying of the material would eliminate much of the time and costs associated with working in the offshore environment. Transportation, and lift boat time accounted for half to three quarters of the costs of the West Delta project. If the decision is made to slurry onshore, appropriate state regulations need to be followed.

Personnel safety and monitoring - Personnel safety should be a primary concern. A site specific safety plan that includes NORM worker protection should be developed and followed. Radiation Safety Officers should be onhand to survey personnel for contamination. In addition the safety officers should watch the personnel for other potential safety and health problems such as overheating. Protective clothing worn by personnel coming in contact with the material is extremely hot. Sufficient breaks should be given to allow for cooling down and resting.

Summary of West Delta project - The West Delta project was one of the first successful NORM disposal operations attempted in the Gulf of Mexico. The project allowed for the evaluation of two techniques in NORM disposal: 1) Injection of a slurry in the tubing casing annulus and 2) Sealing material in casing "capsules" lowered into the wellborel. Although the amount of NORM was relatively small, 36 drums, it validated the procedure and indicated the potential for disposing of greater volumes of material through these methods.

Although successful, the slurry procedure was difficult and encountered problems with grinding and pumping. It required a substantial amount of equipment and personnel to complete. On the positive side, it also had the potential of disposing of a larger volume of NORM material.

Placing the material in casing and running it downhole was effective, took less time and did not require much equipment. The volume of NORM disposed of however, is limited to amount of casing that can be pulled and replaced during the Plug and Abandonment operation.

SOUTH TIMBALIER DISPOSAL PROJECT

The South Timbalier disposal project took place in May of 1993 and involved 31 drums of NORM contaminated materials. Materials disposed of during this project included separator sand, sludge, scale, filters and cut pipe.

Planning - The decision was made to dispose of the 31 drums of NORM material in a project based on the phase 2 casing encapsulation procedure developed in the West Delta project. Two wells were approved by the Minerals Management Service to accept the NORM contaminated material. An additional well was permitted as a backup.

Two wells were permitted based on uncertainty as to the total number of casing joints that would be required to hold the NORM. The amount of casing that each well could accept was dependent on the amount of casing that could be pulled by the crane being utilized in the plug and abandonment operation.

A contractor was identified that was licensed through the state of Louisiana to place the material in casing. A facility inspection of the location was performed. Based on the site visit it was determined that the facility had the capability of performing the operation in a safe and effective manner.

Implementation - All material was encapsulated into 21 joints of 7 5/8" casing. Both ends of each joint were sealed by a steel plate welded into the inside diameter. The joints were then tested for loose contamination. After ensuring there was no contamination the joints were transported offshore for disposal.

Prior to the arrival of the casing, the wellhead was removed and the 7" production casing in the well was pulled to a depth of 1427'. Only one well was prepared based on the amount of casing needed to hold the NORM contaminated material.

The casing was run into the well, lowered inside the 10 3/4" surface casing onto the top of the remaining 7" production casing at 1427' and released using a "J" latch. A Cement retainer was set at 250' below the mudline and a 200' cement plug was set on top. No problems were encountered during the operation.

Summary of South Timbalier project - The ease and efficiency with which the South Timbalier project was implemented showed that sealing NORM contaminated materials in casing is an effective option for NORM

disposal. The project showed improvement over the preceding West Delta project in the following ways.

- Drum cleaning and decontamination was done onshore.
- Only casing had to be transported offshore, reducing transportation cost.
- The material was isolated in casing, reducing onsite contamination risk.
- Running casing was more problem free than pumping and slurrying operations.

CONCLUSIONS

Both the slurry and the casing encapsulation methods are effective methods for permanently disposing of NORM contaminated materials in plug and abandonment operations offshore. Volume of NORM to be disposed of and the design of the plug and abandonment procedure are primary factors to consider when planning the project.

Encapsulation in casing was the more efficient method for disposal of the 30-35 barrels NORM dealt with in the Amoco projects. Handling of the material onshore was easier and more cost effective than dealing with it in the offshore environment. The amount of NORM disposed of by casing encapsulation is dependent on the plug and abandonment procedure. Enough in-place casing must be pulled to make room for the NORM filled casing. If equipment limitations prevent removal of enough casing the slurrying method should be evaluated.

Larger volumes of NORM may be handled more effectively using a combination of the slurry method and casing encapsulation. Costs on a per barrel basis would decrease with larger volumes of NORM. Equipment transportation costs, decontamination costs, and well preparation costs would remain constant, thereby decreasing the cost per barrel disposal expense.

Both methods of disposal require substantial planning effort. Consideration should be given to drumming and cleaning procedures, equipment design, slurry procedures and personnel safety and monitoring plans.

Vitrification of NORM Wastes

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ABSTRACT

Vitrification of wastes is a relatively new application of one of man's oldest manufacturing processes. During the past 25 years vitrification has been developed and accepted internationally for immobilizing the most highly radioactive wastes from spent nuclear fuel. By the year 2005, there will be nine operating high-level radioactive waste vitrification plants. Many of the technical "lessons learned" from this international program can be applied to materials that are much less hazardous, such as naturally occurring radioactive material (NORM).

One NORM soil sample was characterized, and several glasses were made and leach tested. Compared to the original soil, vitrification provided a 67% volume reduction in the sample. The chemical durability of these NORM glasses was comparable to container glass and was superior to Columbia River basalt rock. Based upon the durability of some natural basalt glasses, it can be concluded that the longevity of NORM glasses will remain unaltered in normal environmental conditions for millions of years. Vitrification of the NORM sample will reduce the radon emanation to less than 0.1% of standard construction materials such as brick and concrete. Technically, the vitrified NORM soil can be transformed into useful, saleable products, which could recover a portion of the processing costs. For example, if road barriers could be fabricated from the NORM soils, they could generate about $100 per ton of glass product.

With the deployment of low capital and operating cost systems, vitrification should become a broadly applied process for treating a large variety of wastes. This paper presents a general description of waste vitrification, summarizes its key advantages, and provides test data for a small sample of one NORM to show how waste vitrification may be applied to NORM.

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INTRODUCTION

Vitrification, or glass making, is one of man's oldest industries, dating back nearly 5,000 years (1). Early glasses were not very chemically durable because of the limited technology available then. However, glass artifacts that are nearly 3,500 years old are currently being displayed in museums around the world.

Waste vitrification is a relatively new industry, dating back less than 25 years. This industry has drawn upon past scientific and technical experience. The objective of early waste vitrification was to transform a slurry or sludge containing radioactivity into a solid, chemically durable material. The first radioactive waste vitrification plant started operation in the mid-1980s (2) (3). By the end of the century about nine plants will be processing the most highly radioactive wastes. The merits of vitrification have currently been limited to the most expensive waste streams, such as high-level radioactive wastes. The application of vitrification to other waste streams is in its infancy, but it is believed that it will become a dominant waste management technology in 10 to 15 years.

Waste vitrification is a thermal process that may involve drying, pyrolysis, decomposition of inorganic salts, and the oxidation of metals and carbon; it always involves the melting of oxides. If allowed to reside in the molten pool for sufficient time, this molten oxide material homogenizes and makes a nearly uniform liquid. This liquid can then be cast and, if cooled quickly enough, results in an amorphous solid or glass. Alternatively, through heat treatment, the liquid oxides can be slow-cooled to create different crystalline materials with the potential for a glassy phase--either as a matrix or as an interstitial amorphous phase. Most commercial glasses, flatware, containers, and other glass products sold today are transparent; also, they have few enclosed gas bubbles or seeds and few undissolved oxides or stones. Many precautions are required to achieve these results. Minor additions of various metal ions can alter the color, transparency, and other important material properties. Glasses made from wastes are typically black and opaque due to oxides of iron and other transition metals that are common in nature. A typical glass contains silica as its major constituent. Although other specialized glasses can be made with other materials and techniques, the most common and well-understood is founded upon silica, the most abundant oxide on earth.

Silicate glasses are important environmentally because a broad spectrum of waste materials can and have been incorporated into chemically durable silicate glasses. Studies show that naturally occurring basalt glasses have a very low corrosion rate. Depending on the glass's environment, the alteration or corrosion rate can vary from 0.1 millimeters per million years in arid climates to 10 millimeters per million years in water-saturated environments at average temperatures below 10 degrees centigrade (4). Thus, incorporation of heavy metals or radioactive elements within a silicate glass casting would safely retain these materials for very long periods.

PROCESS DESCRIPTION

Hazardous slurries, solutions, contaminated soils, or miscellaneous solids are fed into the melter using existing technologies. These materials can be either combustible or non-combustible. After entering the high-temperature cavity, the feed material is heated. It first dries, then pyrolyzes if it has organic content. If residual char exists after pyrolysis, it is oxidized by oxygen in the air. When oxidized, the oxides settle toward the molten glass surface, are heated, and eventually melt into the molten pool. This is shown generally in Figure 1.

The heart of the vitrification process is the melter, a refractory-lined cavity with submerged electrodes. After preheating the cavity and the initial charge, the melt becomes electrically conductive. With an alternating current placed between pairs of electrodes, the molten glass is resistively heated. Molten glass temperature is typically limited only by the extent of corrosion resistance and refractoriness in the lining and the electrodes. Temperatures up to 3000°F are sustainable for hazardous waste processing. At these temperatures, almost any material can be melted or dissolved. Small additions of chemicals may be needed to achieve suitable product durability or processability. Local soils, recycled bottle glass, slag, and many other sources can be used as these additives.

A large melter of this type typically has a mean residence time of over 24 hours. Since these melters behave like a well-mixed tank, large variations in the waste feed can be accommodated without dramatically influencing the discharged glass composition. Thus, melters of this type serve to homogenize a heterogeneous waste feed into a time-average of the waste fed. With a suitable off-gas system, the same melter can process many different types of waste and provide a universal "one stop" processing capability.

Vitrification process rates depend on several properties of the waste, such as water content, chemical composition, inherent energy content, and particle size. To achieve the desired process capacity, the surface area of the molten pool is adjusted. For solutions and concentrated slurries, with no exothermic energy in the feed, the specific process rate is between 36 and 60 gal/day/ft^2. For contaminated soils and other inorganic oxide feeds, the process rate ranges between 400 and 600 lb/day/ft^2. For primarily combustible wastes such as municipal solid waste (MSW) or medical waste, over 2000 lb/day/ft^2 is the design value.

Energy requirements depend mostly on the water content and the exothermic energy present in the feed. Typically, 900 kW-hr/ton of glass produced is required to vitrify inorganic material. For contaminated soils, 1600 kW-hr is needed to vitrify each cubic yard (1.76 ton/yd^3). To reduce these costs, innovative energy recovery techniques have been identified for use with the larger processing systems. Where electric energy is either unavailable or too expensive, fossil fuels can be used to melt the wastes being fed. Systems using fossil fuels must address different issues such as particulate entrainment,

heat transmission to the opaque melt, and handling the higher gaseous effluents. However, the net energy needed to melt the waste is the same as for an all electric melting.

ADVANTAGES OF WASTE VITRIFICATION

The primary advantages of waste vitrification are listed below:

1. Incorporates and immobilizes the broadest range of element oxides into chemically durable glass products that can be formed into useful and saleable products
2. Processes solids, slurries, sludges, and mixtures of heterogeneous and physicochemically diverse waste streams
3. Destroys organic compounds and combustible material
4. Provides high volume reduction
5. Produces little or no secondary wastes, returns materials captured in the off gas back to the melter.

One of the most important characteristics of glass is its chemical durability. Few commonly used materials have its versatility. Many times, the chemical resistance of glass can allow it to remain in a corrosive environment for hundreds, thousands, even millions of years. To understand the chemical corrosion resistance of glass, scientists examined some natural glasses that have been in the environment for millions of years. Many basalt glasses have been formed by nature at the earth's surface and under the oceans. Some of these basalt glasses have been in the natural environment for up to 300 million years. Although relatively low in silica, many have endured with moderate to little alteration or corrosion for millions of years. Byers, Jercinovic, et al. (4) have completed an analysis of the natural data and have estimated the alteration or corrosion rates for several basalts under differing conditions.

As shown in Figure 2, the alteration or corrosion rate for these basalt glasses is measured in thousandths of an inch per **million years!** The Columbia River basalt glass has been exposed to mostly an arid climate during the past 12 to 14 million years. The British Columbia and Icelandic basalts were immersed in fresh lake water or under the ocean. Here the corrosion rate is, as expected, higher. However, the corrosion rate of about 0.1" per million years is still very low. These data are valuable for the application of vitrification of wastes. If we make glasses from wastes that have a composition sufficiently similar to these basalt glasses, these natural data provide the confidence that it will endure similar environments with similar results. Thus, the million years' experiments on glass durability completed by nature suggest that many glasses produced from waste should be extremely durable.

To provide perspective on the durability of glass, it is compared to the duration of human civilization in Figure 3. Note that the duration of civilization as represented by the span of written history (~6,000 years) is but a fine line

compared to the endurance of natural glasses. The second bar is the time needed to reduce radium's radioactivity to one millionth of its original, which is about 32,000 years. Less than 1% of the glass would be altered in this time.

Another important characteristic of the waste vitrification process is its practical versatility. The same system can process a diversity of wastes that can be transformed into chemically stable products. To provide a perspective for the different applications of the process, the following list identifies waste streams for which we have completed treatability experiments. All have been transformed into chemically durable glasses. For some situations, the volume reduction achieved during processing of the waste is important. Typical values for some tested materials are shown graphically in Figure 4. The bar chart shows the volume percent of the final glass compared to the original volume.

NON-HAZARDOUS WASTES

Municipal Solid Waste Incinerator Ash
Medical Wastes
Hog Fuel Fly and Bottom Ash
Hog Fuel Pyrolysis and Ash Vitrification
Non-Recyclable MSW Residues
Mass Burn MSW
Combustible and Non-Combustible Construction Debris Solid Wastes
Cardboard Recycling Wastes
10 to 15 Wt% Solids Sewage Sludges

HAZARDOUS WASTES

Foundry Sands
Aluminum Spent Pot Liners
Plating Sludges (FeSO4)
Weapons Components Declassification and Demilitarization
Electric Arc Furnace Dust
Pesticide Contaminated Soils
Paper Recycling De-Inking Sludges
Chemical Weapons and Related Wastes
Electronic Circuits, Old Computers, Terminals, and CRTs
K-Waste Sludges
Hazardous Organic Solutions

RADIOACTIVE

High-Level Radioactive Slurries
Fernald Contaminated Sludges And Soils (OU #1)
Radium-Enriched, High Radon Emanating Soils (Fernald OU #4)
Low-Level Reactor Wastes (Organic Resins, Dry Active Wastes and Sludges)
Weldon Spring Uranium Sludges and Contaminated Soils
Mixed Radioactive and Hazardous Wastes
Plutonium Warhead "Denaturing"
Hanford Low-Level Salt Cake Vitrification (~NaNO3)

VITRIFICATION TEST DATA FOR A NORM SAMPLE

A NORM sample was obtained and characterized using our standard characterization procedures. From these procedures, we were able to characterize the sample as follows:

Fraction lost on drying	0.146
Fraction of dry sample as "sea shells"	0.309
Fraction of dry sample as soil & NORM	0.693
Fraction of dry soil & NORM as organics	0.118
Fraction lost during firing (held at 1200°C)	0.028
Total mass fraction lost	0.354
Approximate volume fraction reduction	0.677

Next, the chemical composition of the dried, oxidized soil was determined. Based on the chemical composition of the soil, several chemical additions were completed to see how the toxic characteristic leach procedure (TCLP) leaching characteristics would vary. These glasses were melted at 1500°C. The chemical composition of these glasses are presented in Table 1. Samples of these glasses were taken, and a modified TCLP test was completed for these glasses. The results of these leach tests for the corresponding glasses are presented in Table 2. The relevance of these results can be better understood by comparing the mass fraction silica losses from these samples to other common materials we have tested. These results are presented in Figure 5. This figure shows that the NORM glass samples are very chemically durable. They are comparable to clear container and Pyrex glasses and are far superior to basalt rock.

Vitrification of NORM materials also provides the significant benefit of nearly eliminating radon and daughter product emissions from the material. After vitrification, radon emanation becomes less than that found in many common construction materials. This fact is shown in Table 3 and is discussed in greater detail by Merrill and Janke (5). Since the K-65 material has a radium content that is over 2,000 times higher, the emanation should be proportionately less. This characteristic is retained as long as the glass is unaltered. Since the glass is very chemically durable, radon retention should be maintained for millions of years for normal environmental conditions.

Since vitrification of NORM waste transforms the material into a chemically durable solid with essentially no radioactive characteristics, there is technical potential of using the discharged material for useful purposes. Sale of products could represent a significant reduction in the processing cost of the NORM soil. For example, if road barriers could be manufactured and sold, the income from this product would be about $100 per ton. Some examples of other potential products from NORM waste material are illustrated in Figure 1.

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Table 1

Chemical composition of an oxidized NORM soil and NORM glasses.
Listed in weight percent.

Oxide	Oxidized NORM Soil	KFW1	KFW2	KFW3	KFW4	RAM1	RAM2	CCC1
SiO2	55.24	49.30	53.24	50.21	46.21	52.60	43.36	51.62
B2O3	*	*	*	*	*	*	17.57	*
BaO	20.26	18.08	18.29	18.41	16.95	19.29	15.90	18.93
Al2O3	7.73	13.15	6.98	7.03	14.43	7.36	6.07	13.77
CaO	5.95	5.31	5.37	5.41	4.98	5.67	4.67	5.56
Fe2O3	5.36	4.79	4.84	4.88	4.49	5.11	4.21	5.01
Na2O	*	4.49	6.35	*	*	4.77	3.93	*
K2O	1.18	1.05	1.06	1.07	0.99	1.12	0.93	1.10
PbO	1.07	0.96	0.97	0.97	0.90	1.02	0.84	1.00
MgO	0.89	0.80	0.80	0.81	0.75	0.85	0.70	0.83
ZnO	0.69	0.62	0.63	0.63	0.58	0.66	0.54	0.65
SrO	0.57	0.51	0.52	0.52	0.48	0.55	0.45	0.54
TiO2	0.44	0.39	0.40	0.40	0.37	0.42	0.35	0.41
P2O5	0.26	0.23	0.23	9.34	8.59	0.24	0.20	0.24
MnO	0.13	0.11	0.11	0.11	0.11	0.12	0.10	0.12
Nd2O3	0.06	0.05	0.05	0.05	0.05	0.05	0.04	0.05
ZrO2	0.05	0.05	0.05	0.05	0.04	0.05	0.04	0.05
CuO	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.03

*Below level of detection.

Table 2

TCLP leachate results for NORM glass compositions of table 1.
Listed in ppm.

Element	Reduced soil melt	Oxidized soil	KFW1	KFW2	KFW3	KFW4	RAM1	RAM2	CCC1
Fe	70.03	*	5.33	9.13	2.49	3.78	11.18	7.99	8.79
Ba	106.18	1.41	1.23	1.29	1.19	5.34	2.96	1.76	1.20
Si	0.33	0.42	0.75	0.43	0.47	0.76	0.56	0.47	0.56
Ca	41.06	2,025.	0.65	0.37	1.70	4.74	1.07	0.70	0.55
Sr	1.92	5.96	0.04	0.04	0.07	0.32	0.09	0.05	0.04
Mn	1.13	*	0.05	0.05	0.03	0.06	0.07	0.05	0.06
Zn	1.52	0.60	0.01	0.01	0.02	0.07	0.08	0.04	0.02
P	0.09	*	*	*	0.65	2.86	*	*	*
K	2.50	*	*	*	*	*	1.79	*	*
B	*	*	0.13	*	*	*	*	0.41	*
Al	0.12	*	0.32	*	0.18	*	*	*	0.33
Mg	0.20	*	0.09	*	0.10	0.31	0.14	0.10	0.10
Cu	*	*	0.10	0.04	*	*	*	*	0.04
Nd	0.07	4.78	0.01	*	*	*	0.04	0.03	0.01
S	2.50	484.65	*	*	*	*	*	*	*

* Below level of detection.

Table 3

Comparison of radon emanation and radium content of different materials.

Material	Radium Concentration (pCi/g)	Radon Emanation Rate (pCi/m^2/s)
Concrete	0.3 - 2.2	0.02 - 0.22
Alum Shale Concrete	10 - 70	0.4 - 1.5
Brick	0.5 - 5	0.02 - 0.04
Vitrified K-65 Material	2×10^5 - 3×10^5	0.01 -0.06
NORM Soil	~100**	~4**
Vitrified NORM Soil	~100**	~0.00001**
Regulatory Limit		20

** Values not measured but extrapolated from existing data

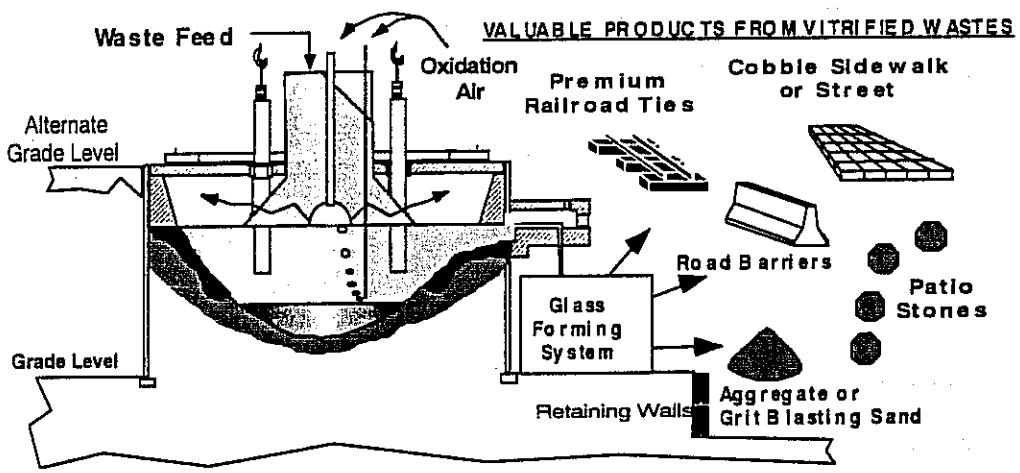

Figure 1. Schematic of the Terra-Vit waste vitrification process.

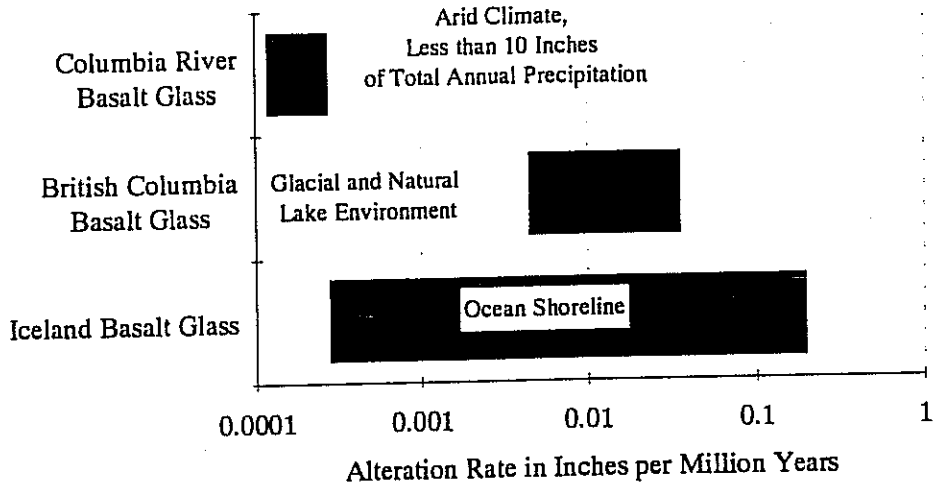

Figure 2. Alteration or corrosion rate for natural basalt glasses under differing environmental conditions.

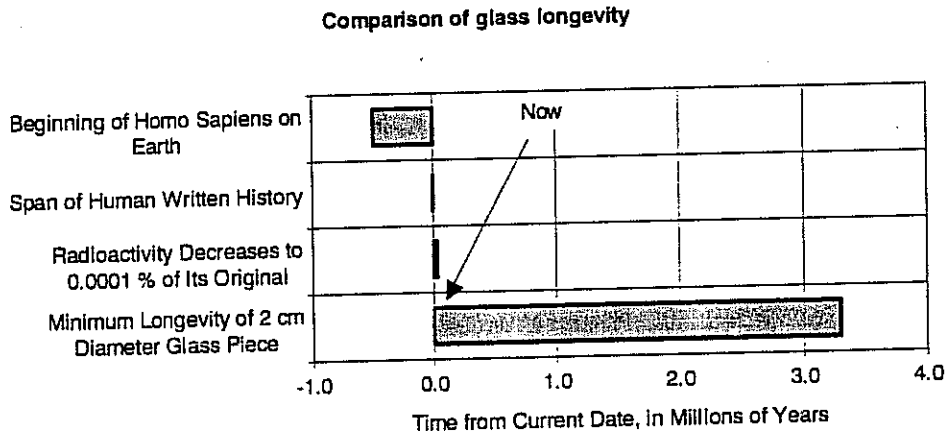

Figure 3. Comparison of glass endurance.

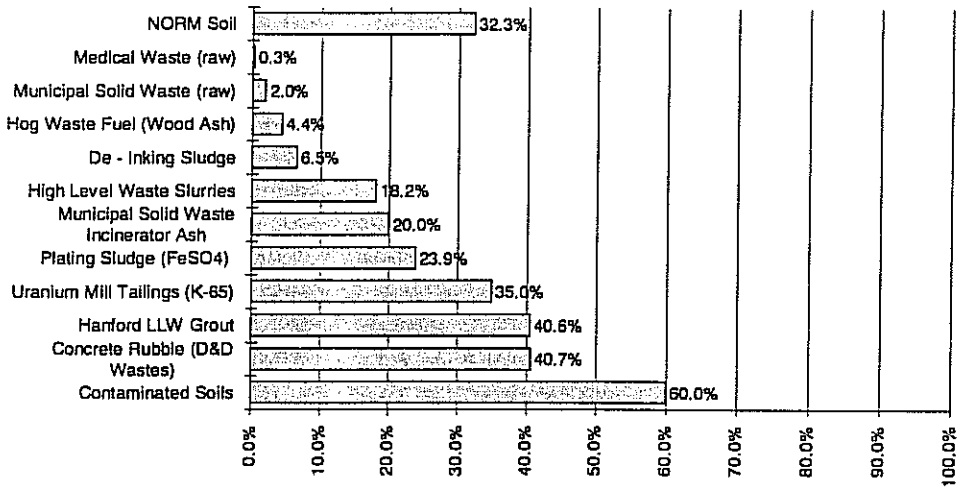

Figure 4. Volume percent of vitrified product compared to the original waste volume.

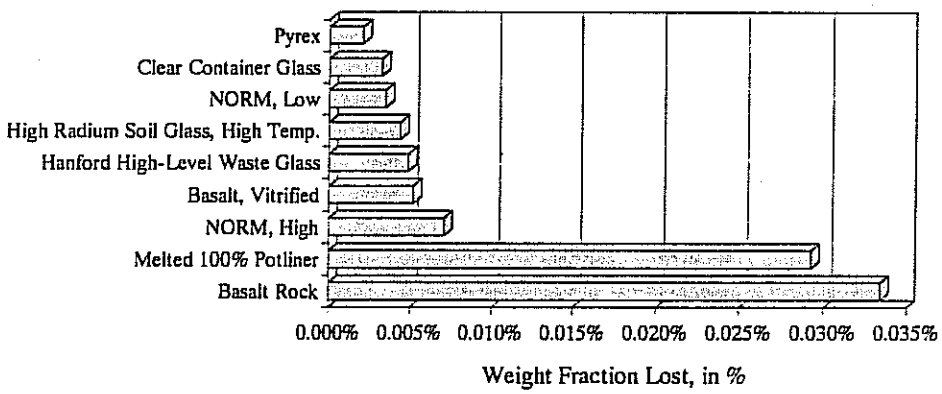

Figure 5. Comparison of different material's weight fraction silica lost in TCLP test. "NORM, Low" and "NORM, High" are the lowest and highest values measured, respectively.

Segregation of Radium from Scales and Process Vessel Solids

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Radium enriched scales and sludges can precipitate in oil and gas production tubulars and process vessels. Recently adopted regulations in Louisiana and elsewhere classify such materials as NORM (naturally-occurring radioactive materials) waste. NORM waste disposal is both expensive and complex. Since the cost of disposal is nearly proportional to waste volume, there is great interest in methods of reducing this volume.

In the work presented here, experiments were conducted with a commercial scale dissolver, containing the complexing agent diethylenetriaminepentaacteic acid (DTPA) and oxalate, and a sample of process vessel sludge that was primarily barite. Dissolution of the barite sludge was slow, even at elevated temperature (80°C). The oxalate ion permits the efficient co-precipitation of the radium with barium oxalate upon acidification of the leachate. This chemistry may permit NORM waste reduction.

The feasibility of separating radium from barium in the leachate was considered. Previous workers have shown that the complexing agent ethylenediaminetetraacetic acid (EDTA) should allow radium to be recovered selectively on a cation exchange resin. However, experiments described below indicate that the DTPA in the commercial scale dissolver does not discriminate sufficiently between the two metals to allow for the separation of radium and barium in this manner.

INTRODUCTION

As a result of changes in temperature and pressure and/or mixing with other waters, solids may precipitate from water co-produced with oil and gas. These solids accumulate inside tubulars as scale or on the bottom of process vessels (tanks, separators) as sludge. In certain regions, these solids may exhibit substantial concentrations of radium. When present at high enough levels, these solids may, in some jurisdictions, be regulated as NORM (naturally occurring radioactive materials) wastes. When NORM is present, descaling of tubulars and cleaning and decommissioning of process vessels must be undertaken with heightened concern for worker safety and environmental protection.

At present, NORM waste can be placed in special landfills or entombed in wells scheduled for plugging and abandoment. Disposal by deep well injection has also been considered (1). Regardless of the method of disposal, disposal costs are nearly proportional to waste volume. Since these costs are high ($300 to $1,000 / drum; waste life cycle cost), techniques for reducing the volume of NORM waste are highly desirable. Physical methods such as washing to remove oil and sieving to remove water have proven to be only partially successful (2). Attention is now turning to chemical methods. This paper describes efforts to dissolve a radium containing process vessel sludge and to separate the radium from barium in the leachate.

The dissolution of barite scales in oilfield equipment has been considered previously. Patents relating to barite scale dissolvers began to appear in the early 1970's. Recently, researchers at Mobil Research and Development Corp. have patented several innovative formulations (3). These utilize the complexing agents ethylenediamintetraacetic acid (EDTA) or diethylenetriaminepentaacetate (DTPA).

Higuchi, *et al* (4) have described a method for separating radium from barium that also utilizes EDTA. These workers found that an EDTA solution was capable of eluting a variety of metals ions (e.g. Sr^{2+}, Ba^{2+} and Ra^{2+}) adsorbed onto a strongly acidic cation exchange resin. Eluent selectivity could be controlled by pH adjustment. For example, at pH = 9.0, Sr^{2+} and Ba^{2+} were eluted but Ra^{2+} was retained on the resin. The elution data from Higuchi, *et al* (4) are summarized in Table 1.

The results of Higuchi, *et al* (4) suggest that if an EDTA solution containing both Ba^{2+} and Ra^{2+} is adjusted to a pH of 9.0 and then passed through a cation exchange column, most of the Ra^{2+} will be retained on the resin. This approach is similar to that of the complexation-assisted ion recovery (CAIR)

process being developed for the removal of heavy metal ions from industrial wastewater (5). The primary objective of the work described below was to determine if the CAIR process was capable of separating Ra^{2+} from Ba^{2+} in "spent" scale dissolver.

EXPERIMENTAL MATERIALS AND METHODS

Except as indicated, all solutions were prepared with reagent grade chemicals and high-purity deionized water produced with a Milli-Q system (Millipore Corp.). Pyrex glassware was used in all reactions and in the preparation of solutions for analysis. For extended storage, solutions were transferred to polyethylene bottles.

The process vessel sludge material used in the experiments was obtained from the clean-out of an in-service separator operating in the western Gulf of Mexico. As received, the material was comprised of fine to very fine sand sized particles having a reddish brown color and a slight hydrocarbon odor. The material contained some water extractable chloride. Bulk chemical analysis of the sludge was carried out by X-ray fluorescence spectrometry (XRF). These analyses were performed by a commercial laboratory (XRAL, Ontario, Canada). Selected data from this analysis are presented in Table 2. The sludge is largely barite (Ba as BaO = 60.7 wt.%; Ba as $BaSO_4$ = 92 %), but contains a significant amount of strontium (19,900 ppm) and minor amounts of lead, copper, zinc cobalt, nickel, antimony and arsenic.

The commercial scale inhibitor, marketed under the tradename Barrage™, was obtained from Baker Performance Chemicals. As received it was a clear, colorless, viscous liquid with a pH in excess of 13. This product is a proprietary mixture of the complexing agent DTPA, oxalate ion, potassium hydroxide and possibly other components.

Analysis of solutions for barium and iron was performed by flame atomic absorption spectrophotometry (FAAS). Instrument conditions used for barium were: λ = 553.6 nm, slit = 0.7 mm, acetylene-nitrous oxide flame. Standard solutions were matrixed matched to samples. This was especially important because the samples contained very high levels of potassium. When high levels of alkali metals are present, barium ionization in the flame is suppressed and the signal corresponding to elemental barium is enhanced. Instrument conditions for iron analysis were: λ = 248.3 nm, slit = 0.2 mm, acetylene-air flame.

Radium was semi-quantified by NaI γ-spectrometry. The system used was a 4x5 Bicron well detector, contained in an 8" steel shield, coupled to a PCAII multichannel analyzer, power supply and amplifier (Oxford-Tennelec). The large crystal size, 4π geometry, and low backgound permitted rapid counting of the small sample masses (5-25 g) generally available. All count data were background subtracted. Radium activity was inferred by integrating the ^{214}Bi peak at 609 keV. All samples were contained in low-density polyethylene vials during counting. It should be stressed that the data generated by this method are approximate. No attempt was made to account for in-growth of radium daughters except for conducting the counting experiments at a relatively constant time after completing the solution experiments.

The cation exchange resin used in these experiments was Amberlite IR-120 plus (Rohm & Haas). While nominally in the Na^+ form, this material exhibited a residual acidity, which was eliminated by contacting the resin with an excess of a 10% NaOH solution, then washing with high-purity water until a pH value of 9.0 was obtained. The resin was contained in polyethylene columns (Nalgene), and was retained in the columns with glass wool.

EXPERIMENTS CONDUCTED AND RESULTS

Dissolution of the Barite Sludge

The goal of this set of experiments was to examine the dissolution behavior of the barite sludge in Barrage™ scale dissolver. A 20.0 g sample of the sample material was sequentially extracted with 50.0 mL aliquots of Barrage™. The extractions were conducted at 80°C with vigorous stirring. After each extraction, the leachate was filtered through No. 42 Whatman paper, and a subsample was diluted with 2% HNO_3 and then analyzed for barium by FAAS. After four extractions using this protocol, the remaining solid material was treated with a hydroxylamine solution (0.040 M in hydroxylamine hydrochloride and 25 vol.% in acetic acid) to dissolve hydrous metal oxides and release any metal ions that are adsorbed onto or coprecipitated with these phases (6). As before, this extraction was carried out at 80°C with vigorous stirring. The liquid phase quickly turned yellow, indicating the removal of ferric ion from the solid. Simultaneously, the solid phase changed from reddish-brown to a pale tan. After allowing the solids to settle, the liquid was decanted off. Finally, the remaining solids were extracted with 250 mL of Barrage™.

The results of the successive extraction experiments are presented in Table 3. When 50 mL of Barrage™ was utilized, the amount of barium extracted was greater after 10 hours of extraction than after 4 hours. The amount of barium extracted also increased when the volume of barrage™ was increased from 50 to 250 mL. Leaching with the hydroxylamine solution extracted much iron but little barium. This leachate was also subjected to γ-spectrometry. No activity in excess of background was observed.

Feasibility of the Separation of Radium and Barium in Barrage™

The goal of the second set of experiments was to determine the feasibility of achieving the separation of radium from barium in Barrage™ scale dissolver by complexation-assisted ion recovery. The experiments were conducted in three parts: 1) determination of the pH range over which the Ba^{2+}-DTPA complex destabilizes, 2) determination of the consequences of acidifying Barrage™ containing barium, and 3) examination of the cation exchange behavior of Barrage™ used to dissolve some of the experimental sludge.

The pH range over which the Ba^{2+}-DTPA complex destabilizes was studied using a solution that was 0.10 M in Ba^{2+} and 0.20 M in DPTA. Initial solution pH was adjusted to 8 by the dropwise addition of 50 wt.% NaOH. This solution was then passed at 5 mL/min through a column containing the cation exchange resin. Eluant from the column was collected, and its pH was measured. A 10 μL aliquot was withdrawn, diluted with 2% HNO_3 and analyzed for barium by FAAS. The remaining eluant was acidified by the addition of several drops of concentrated HCl and then passed through the cation exchange column again. The amount of barium in the eluant was used to calculate the fraction retained on the resin when the solution was passed through the column.

The results of this experiment are presented in Fig. 1. It can be seen that the retention curve for DTPA is to the left of the EDTA data (4), an indication that the stability of the Ba^{2+}-DTPA complex is greater than that of the Ba^{2+}-EDTA complex. No barium is retained on the resin at pHs $\geq$ 7.9.

To investigate the consequences of acidifying "spent" Barrage™ scale dissolver, a concentrated $BaCl_2$ solution was combined with the scale dissolver to produce a solution that was 0.1 M in barium. When the pH of this solution was reduced below 7.5 by the addition of concentrated HCl, a white precipitate formed. Analysis of the liquid indicated that barium had been incorporated into the solid. Reaction of the precipitate with an acidic potassium permanganate solution yielded a gas, indicating that it also contained oxalate.

The precipitation noted above was studied further by acidifying portions of the leachates produced in the sludge dissolution experiments described above. The leachates were acidified to a pH of 6.5 and immediately filtered. The filtrates were then analyzed for barium by FAAS. These data were used in conjunction with the barium concentrations observed in the original leachates to calculate the percentage of barium remaining in the liquid phase. These results are presented in Table 4. In addition, γ-spectrometry revealed that radium was effectively co-precipitated with the barium.

The precipitation of barium oxalate is an indication that the Ba^{2+}-DTPA complex has begun to be destabilized by the added acid. To determine if the Ra^{2+}-DTPA complex is destabilized at somewhat higher pHs, a portion of a sludge leachate was acidified with concentrated HCl to a pH of 7.6 (0.1 pH units above the value at which barium oxalate precipitates). This solution was passed through a cation exchange column, and both the eluant and the resin were examined for the presence of radium by γ-spectrometry. The resin showed no activity above background.

DISCUSSION

Dissolution of the Barite Sludge

Dissolution of the barite sludge with Barrage™ scale dissolver was painfully slow. The results presented in Table 3 suggest that after 4 hours at 80°C, the reaction had progressed to only 60% of completion (assuming that the system was at equilibrium after 10 hours). Paul (7) described dissolution studies involving both reagent grade barium sulfate and a field sample of barite scale. While the reagent-grade material dissolved fairly quickly (particularly in the presence of oxalate), the barite scale was much more resistant to dissolution. The reasons for this disparity in dissolution kinetics between pure barium sulfate and barite scale were not discussed.

From the data in Table 3, complete solubilization of a metric ton of barite would require approximately 14,700 liters (3,900 gal) of Barrage™ scale dissolver. An enhanced rate of dissolution was observed when a significant excess of the scale dissolver was present in the reaction mixture (extraction no. 5).

Radium ion can adsorb to hydrous ferric oxide. The barite sludge sample contained some iron (by XRF analysis), was a reddish-brown color characteristic

of iron oxides, and gave a positive reaction when leached with a hydroxylamine hydrochloride - acetic acid solution. Even so, no radium was detected in the resulting leachate. Thus, in this sample radium was not associated with hydrous ferric oxide. Furthermore, the presence of ferric oxides in the sludge did not effect substantially barium dissolution by Barrage™.

Feasibility of the Separation of Radium and Barium in Barrage™

Complexation-assisted ion recovery of radium from a mixture of radium and barium in Barrage™ scale inhibitor is not feasible. The failure of the cation exchange resin to retain a detectable amount of radium activity when the leachate was adjusted to pH = 7.6 indicates that there is little difference between the stability of the DTPA complexes of Ra^{2+} and Ba^{2+}. Consistent with this observation, Sillen and Martell (8) list the stability constant for Ba^{2+}-DTPA as 4.0×10^8, and for Ra^{2+}-DTPA as 3.2×10^8.

Possibility of Remediation of Diffuse NORM Waste

Chemical washing of diffuse NORM from sludges and soils may be possible using a solution similar to the commercial scale dissolver Barrage™. Leachates from the sludge, when acidified to pH = 6.5, lost over 98 wt.% of their barium as barium oxalate precipitate. Radium activity was similarly removed from the solution. Thus, it is conceivable that diffuse NORM could be removed from sludges and soils, resulting in a significant reduction in volume of hazardous material.

CONCLUSIONS

The commercial scale dissolver Barrage™ will dissolve barite sludge, liberating both barium and radium to solution. However, the kinetics of the dissolution reaction are slow. Even with elevated temperature (80°C), vigorous mixing, and a relatively fine-grained solid, the reaction was only 60% complete after 4 hours. The rate of reaction increased slightly when a large excess of scale dissolver was present.

Separation of radium from barium in the commercial scale dissolver via the complexation-assisted ion recovery process is not feasible. The stability constants

for the Ba^{2+}-DTPA and Ra^{2+}-DTPA complexes are not sufficiently different.

The removal of radium from diffuse NORM (e.g. dilute sludges and contaminated soils) by chemical leaching with commercial scale dissolver may be economically feasible. When a solution of Barrage™ containing both barium and radium is acidified, a barium oxalate precipitate is formed. Radium is coprecipitated with this material. At pH = 6.5 over 98% of the barium was removed from the solution, and the amount of radium remaining in the solution was not detectable.

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Table 1

Stability constants (8) and % retention on a cation exchange resin as a function of the pH of the EDTA eluant (4).

	EDTA	% metal retained vs. pH			
metal ion	log K values	10	9	8	7
Sr^{2+}	8.6	0	0	0	80
Ba^{2+}	7.8	0	0	90	100
Ra^{2+}	7.1	0	90	100	100

Table 2

Compositional data for the barite sludge sample obtained by X-ray fluorescence analysis (duplicate analyses, not all analytes shown).

Analyte		Abundance	
BaO	(%)	60.7	60.4
S	(%)	14.5	14.3
Sr	(ppm)	19,700	19,900
Pb	(ppm)	393	380
Zn	(ppm)	253	254
Sb	(ppm)	63	64
Ni	(ppm)	38	35
As	(ppm)	12	12
Co	(ppm)	11	9

Table 3

Dissolution of 20 g sample of barite sludge in successive 50 mL aliquots of Barrage™ at 80°C.

extract no.	extraction time (hr)	Ba extracted (g)
1	4	1.3
2	4	1.1
3	10	2.0
4	4	1.5
5*	4	2.8

* leached with 250 mL of commercial scale dissolver, following extraction of hydrous metal oxides.

Table 4

Barium remaining in the liquid phase following acidification of the leachate.

filtrate no.	Ba remaining (%)
1	1.8
2	1.7
3	1.5
4	0.4

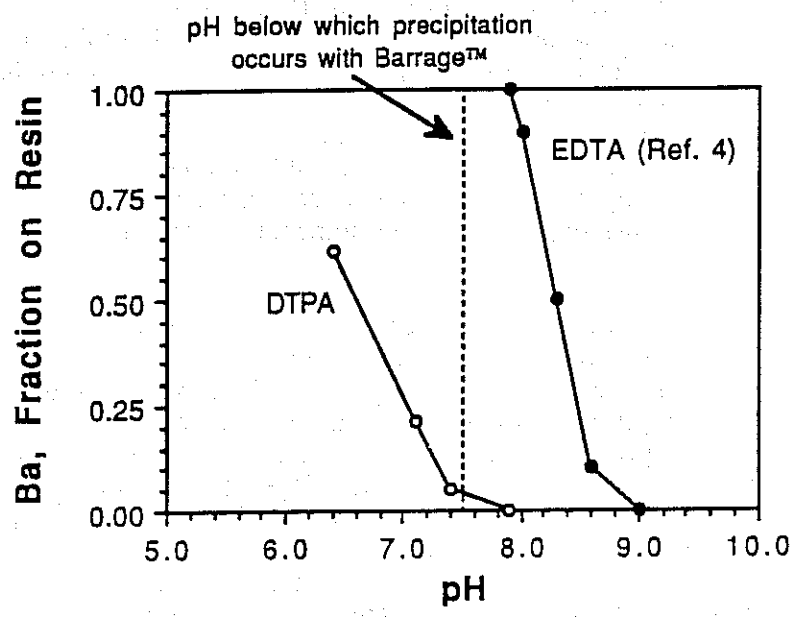

Figure 1. Effect of the pH of the DTPA solution on the retention of Ba^{2+} on the cation exchange resin.

NORM Waste Minimization Using In-Situ Treatment Method

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ABSTRACT

Groundwater Services, Inc. (GSI), and researchers at the University of Houston (UH) have developed a new in-situ technology for removing naturally-occurring radioactive materials (NORM) from reservoir fluids prior to their entry into oil, gas, or water production wells. The method retains NORM within the subsurface by means of highly-selective radionuclide sorbents deposited within the reservoir matrix surrounding the well. Bench-scale studies have demonstrated in-situ removal rates of over 99.99% for radium and other contaminants. This in-situ immobilization technique significantly lowers NORM concentrations produced at ground surface, thereby reducing NORM waste disposal or treatment costs, as well as the risk of human exposure or environmental contamination.

The treatment method involves placement of stable, highly-selective radionuclide sorbent compounds within the reservoir matrix using either in-situ precipitation or high pressure injection techniques (see Figure 1). Dissolved radionuclides within groundwater flowing through the treated aquifer zone are removed by means of ion exchange, adsorption, chelation, chemisorption, or coprecipitation onto the sorbent solids (Connor, Clifford, King, 1993a). Given the low mass concentrations of radionuclides commonly present in reservoir fluids (i.e., part-per-trillion range) and their extreme affinity for the selected sorbents, relatively small quantities of the sorbent solids (i.e., part-per-million range) serve to immobilize dissolved NORM without significantly impacting reservoir porosity (Connor et al, 1993a). Sorbent agents shown to be effective for this application include fine-grained ion-exchange resins, functionalized and non-functionalized polymeric adsorbents, zeolites, and a broad range of inorganic oxide, hydroxide, sulfate, carbonate, and phosphate compounds Following placement, such compounds are retained within the reservoir due to electrostatic attraction or chemical bonding to the solid matrix surface, establishing a large-capacity, in-situ "filter" for dissolved radionuclides. The appropriate in-situ sorbent agent for a given site depends on the radionuclide(s) of concern and local reservoir conditions (see Table 1). At a given well site, the chemical composition, concentration, and dimension of this in-situ "filter" can be adjusted to achieve NORM removal for an extended time period.

In-situ immobilization of radionuclides offers significant advantages over conventional water treatment methods or scale control techniques. Several traditional water treatment technologies have been shown to be capable of removing dissolved radium or uranium from produced water (Clifford, 1990); however, all such above-ground treatment processes involve generation of a

concentrated radioactive waste residue, which presents significant human exposure and waste disposal problems. In-situ removal of radionuclides achieves NORM waste minimization by reducing NORM levels in produced water and minimizing the potential for radioactive scale formation in production and distribution piping. Due to the trace quantities of sorbent solids required for in-situ radionuclide removal, the method furthermore avoids the porosity reduction and production loss problems associated with scale inhibitor "squeeze" methods.

A full-scale demonstration of this treatment method is presently underway for a community water supply well in Houston, Texas, under sponsorship from the State of Texas Advanced Technology Program. Concurrently, the research team is pursuing a phased test program to develop guidelines for application to oil and gas wells. On the basis of work completed to date, a patent for this in-situ treatment technology was issued to GSI by the U.S. Patent Office in March 1993 (U.S. Patent No. 5,196,124; Connor, Clifford, and King).

NORM OCCURRENCE, REGULATION, AND TREATMENT COSTS

NORM Concentrations in Oil and Gas Reservoir Fluids

Naturally-occurring radioactive materials (NORM) have been found to be present as dissolved ions within brine fluids produced from both oil and gas production wells. Radioactive isotopes are contained in varying concentrations within the solid matrix of all rock and soil formations and are released to subsurface pore fluids by the processes of dissolution, desorption, or radioactive decay. The resultant concentrations of dissolved radionuclides at any location within the reservoir is dependent upon relatively complex geochemical factors including the composition of the parent rock, the reservoir porosity, the residence time of the pore fluid within the formation, and the isotope solubility and half-life duration (Aieta, 1987; King et al, 1989; Lowry et al, 1988).

The predominant radionuclides of concern within oilfield reservoirs are compounds in the uranium (U) and thorium (Th) decay series, specifically radium (^{226}Ra and ^{228}Ra), uranium (^{238}U and ^{234}U) and radon (^{222}Rn). Radium isotopes represent the principle radionuclides of concern in produced waters due to their prevalence, duration, and tendency to become concentrated within scales and residues. Dissolved radium concentrations in produced waters vary significantly depending on site-specific reservoir characteristics. As shown on Table 1, the results of a 1990 survey conducted by the Offshore Operators Conference show ^{226}Ra and ^{228}Ra levels to range from 4.1 to 584 pCi/L and 18 to 586 pCi/L, respectively, within brine samples collected from 42 offshore platforms in the Gulf of Mexico (Stephenson et al, 1990). Comparable ^{226}Ra values (i.e., 10 to 785 pCi/L) have been measured in prior surveys of geopressured brines associated with gas production wells (O'Day et al, 1987).

Health Effects and Related Regulatory Standards

Excessive human exposure to radioactive materials has been shown to have both mutagenic and carcinogenic effects (Milvy et al, 1990). The incidence of such health impacts depends on the intensity and duration of actual exposure. Ingestion of radionuclides represents a critical concern due to the effects of long-term radionuclide retention within body tissue. In oilfield operations, coprecipitation of radium and barium sulfate from produced waters can result in radioactive scale formation within piping, heat treaters, and brine tanks - posing a risk of worker exposure or environmental contamination during equipment inspection and repair or pipe cleaning operations (API Bulletin E2, 1992). Radon gas present in natural gas streams not only accumulates within gas processing units but can deposit a thin film of radioactive ^{210}Pb on the interior surface of distribution piping and equipment.

In 1976, the U.S. EPA established Maximum Contaminant Levels (MCLs) for ^{226}Ra, ^{228}Ra, and gross alpha and beta radiation levels in drinking water, and has recently proposed expanding these health standards to include both uranium and ^{222}Rn (AWWA, 1991). No federal regulations have yet been promulgated governing the handling and disposal of NORM-contaminated materials from the oil industry. However, in the past two years, Texas, Arkansas, Mississippi, Louisiana, and Michigan have proposed and/or implemented NORM management regulations specifying worker protection standards, soil and equipment testing procedures, and property transfer restrictions for oil and gas production facilities and other industries involved in the production, transport, storage, or processing of NORM or NORM-contaminated material. At present, the EPA is also considering the establishment of NORM effluent limitations for produced waters discharged from offshore oil and gas facilities.

Conventional NORM Treatment Processes and Related Costs

Produced water, consisting of highly concentrated brines with varying concentrations of dissolved NORM, is generated in conjunction with oil at nearly all oil production wells, in volumes ranging from 50% to over 95% of the total fluid stream (Caudle, 1994). Annually, over 21 billion barrels of brine and 2.5 billion barrels of oil is produced in the United States (Wilson, 1994). At most onshore oilfields, the produced water stream is processed for reintroduction into the oil and gas reservoir via brine injection wells (Lawrence et al, 1994). At offshore facilities, produced water may be disposed into the ocean, following pretreatment for control of oil and grease and other general water quality parameters. When present within the produced water stream, dissolved NORM constituents (principally radium) will result in radioactive scale formation on piping and equipment, radioactive sludge within produced water treatment plants, and, at offshore facilities, overboard discharge of NORM contaminants.

Current strategies for management of NORM-contaminated waters or waste materials include traditional water treatment technologies (ion exchange, lime softening, reverse osmosis); removal and deepwell injection of radioactive scale

solids; and use of scale inhibitor agents. Estimates of the costs of such NORM waste processing and disposal methods range from $8 per barrel to over $1800 per barrel of NORM waste, depending on location and available disposal options (Wilson, 1994). The economic, safety, and environmental concerns associated with management and disposal of these waste materials pose a significant impediment to the widespread application of conventional, above-ground NORM treatment processes within the oil industry.

APPLICATION IN-SITU NORM TREATMENT METHOD TO PRODUCTION WELLS

Placement of In-Situ Radionuclide Filter

For the purpose of this in-situ treatment method, a sorbent solid is either a) precipitated within the reservoir matrix by the reaction of two or more carrier solutions or b) directly introduced into the reservoir as a solid phase component of a solid-liquid slurry using high pressure injection techniques (see Figures 2 and 3). The optimal procedure for deposition of the sorbent solid within the reservoir depends upon the chemical and physical characteristics of the reservoir pore fluids and solid matrix (see Table 1). In-situ precipitation of the sorbent solid can best be applied within reservoirs containing fresh to moderately saline groundwater, such as those which are commonly exploited for water supply purposes. Within oil or gas production reservoirs containing complex, highly reducing aqueous solutions and/or multiphase fluids, direct injection of the sorbent solids using hydraulic fracturing or gravel-packing techniques can provide practical advantages in terms of the distribution and stability of the sorbent solid within the reservoir matrix.

Applicable Radionuclide Sorbents

For in-situ NORM removal, the sorbent agent must be a stable solid with a high affinity for radium, the principal radionuclide contained in subsurface reservoir fluids. Within fresh water environments, in-situ precipitation of MnO_2 by reaction of complementary solutions of $KMnO_4$ and $MnSO_4$ has been shown to establish an effective in-situ filter for dissolved radium (Connor et al, 1993a). The solid MnO_2 precipitated onto aquifer sands has a negatively charged surface, which attracts the divalent radium ion (Ra^{2+}) in addition to other ions. In fresh water, the order of affinity of common cations for sorption onto MnO_2 is as follows:

$$Ra^{2+} > Ba^{2+} >> Sr^{2+} > Ca^{2+} > Mg^{2+} >> Na^{+}.$$

Thus, if significant concentrations of the Ba^{2+} ion are present in the water, fewer sites will be available for Ra^{2+} sorption onto the MnO_2 solid. Generally, however, the concentrations of competing ions in fresh or slightly saline waters is not high enough to seriously inhibit the uptake of radium. Consequently, solid MnO_2 or other such stable precipitates (e.g., iron hydroxide; aluminum hydroxide; phosphates of zirconium and calcium; oxides of zirconium, titanium,

antimony, and tin; etc.) represent feasible NORM sorbents for application in water supply aquifers.

Within the highly concentrated brines encountered in oil and gas reservoirs, concentrations of competing ions such as Ba^{2+}, Sr^{2+}, and Ca^{2+} will likely interfere with radium uptake on MnO_2. In addition, the anaerobic, highly-reducing conditions existing in such brine reservoirs can affect the formation and stability of such precipitates. For example, in anoxic and anaerobic environments, a solid MnO_2 (Mn(IV)) precipitate will revert to soluble manganese (Mn(II)) ions, thereby dissolving the sorbent and freeing any sorbed radium.

For placement within oil and gas reservoirs, stable radium sorbent agents can be impregnated within polystyrene resins and either applied as a resin coating to proppant sand or gravelpack material or directly injected as polystyrene beads. Polystyrene resin coated sands and beads have been previously employed as hydrofracturing proppants and found to provide significant advantages in terms of proppant transport and strength (Economides et al, 1989). Radium sorbent agents that can be applied to oil and gas reservoirs in this manner include:

- Macroporous Ion Exchange Resins: Macroporous, highly cross-linked polystyrene resins impregnated with sulfonate or carboxylate functional groups have been found to exhibit a very high affinity for dissolved radium even in the presence of competing ions (Clifford et al, 1988).

- Barium-Sulfate Impregnated Resins: Pure $BaSO_4$ crystals have an exceptional capacity for sorbing radium from brine solutions, as demonstrated by the formation of Ra-$BaSO_4$ scales in oil production piping. Macroporous cation resins impregnated with $BaSO_4$ crystals have been experimentally marketed by the Dow Chemical Company as XSF 43230 resins and have been found to provide radium removal capacities in excess of 100,000 filter bed volumes in laboratory studies (Clifford et al, 1988).

- Crown-Ether Functional Groups: Proppant sands functionalized with radium-selective crown-ether functional groups represent a third possible sorbent agent for oil reservoir applications; however, such compounds are significantly more costly than the resin-based agents.

Based on laboratory analyses conducted to date, the ideal radium sorbent agent can be expected to produce over 100,000 barrels of radium-free produced water for each barrel of sorbent material placed in the formation (Connor et al, 1994).

RESEARCH AND DEVELOPMENT PROGRAM

Since 1987, the University of Houston (UH) has conducted extensive EPA-sponsored research regarding radionuclide treatment technologies (Clifford et al, 1988; Subramonion et al, 1988; Clifford, 1990; Clifford and Zhang, 1994; Zhang and Clifford, 1994). In 1989, GSI and UH teamed to develop techniques for

subsurface application of radionuclide removal agents (Connor et al, 1993a). On the basis of work completed to date, a patent for this in-situ treatment technology was issued to GSI by the U.S. Patent Office in March 1993 (U.S. Patent No. 5,196,124; Connor, Clifford, and King, 1993b). On-going research and development efforts are summarized below.

Treatment of Water Supply Wells

Laboratory Study: During the period of 1989 to present, GSI and UH have conducted a series of laboratory tests to demonstrate the feasibility of depositing sorbent solids within subterranean reservoirs as an in-situ filter for radium removal. For this purpose, glass columns were loaded with a natural silty sand soil, treated to deposit a radionuclide-sorbent material within the soil matrix (i.e., MnO_2), and subsequently rinsed with groundwater containing naturally-occurring ^{226}Ra. Analysis for column effluent liquids showed the treated sand columns to achieve significant radionuclide removal efficiencies in comparison to untreated sand. As shown on Figure 4, the radium concentrations in the effluent of a MnO_2-treated column was still non-detected after over 11,000 bed volumes of groundwater had been passed through the column. For a water supply well treated over a 25 ft radius surrounding a 100 ft screen length, this radium removal capacity would correspond to treatment of over 4 billion gallons of produced water prior to radium breakthrough (see Figure 5).

Field Demonstration: A full-scale field demonstration of this in-situ radium removal method is presently being commenced under sponsorship from the State of Texas Advanced Technology Program (ATP). The test site consists of a 1100 ft deep, 1000 gpm capacity drinking water supply well located in Houston, Texas. The well was removed from service in 1986 due to dissolved radium concentrations in excess of 20 pCi/L. The demonstration study will involve: 1) sampling and testing of each screened interval within the well to identify radium and uranium producing zones, 2) optimization of the in-situ precipitation process by means of preliminary groundwater modeling, 3) placement of an in-situ MnO_2 filter within the selected production zone(s), and 4) monitoring of well discharge for a one-year operating period to measure the radium removal capacity.

Treatment of Oil and Gas Wells

For application of this in-situ NORM treatment method to oil and gas production wells, research efforts must address the following issues: 1) effects of competing ions in brine solutions, 2) potential effects of dissolution-precipitation phenomena, high temperature, and multi-phase fluids within the reservoir environment, and 3) optimal procedures for sorbent placement using hydrofracturing or gravel-packing techniques. For this purpose, GSI and UH are presently pursuing a phased research program involving the following steps:

- *Stage 1 - Preliminary Screening of Sorbent Agents*: Conduct radium adsorption isotherm tests in synthetic and actual oil well brines using various sorbent agents. Test thermal stability amd multi-phase fluid effects on the most radium-selective sorbents.

- *Stage 2 - Preparation and Testing of Proppant Materials*: Develop and test sorbent-treated proppant or gravelpack materials, including i) sorbent-impregnated polystyrene beads and ii) silica sand particles treated with a crown ether or macroporous polymer surface coating.

- *Stage 3 - Field Demonstration*: Inject treated proppant or gravelpack material into reservoir zone surrounding production well to evaluate in-situ radium removal from produced brine.

BIOGRAPHICAL INFORMATION

- **Mr. John A. Connor, P.E.** Mr. Connor, President of GSI, received an M.S. in Civil Engineering from Stanford University and has over 14 years of professional experience in geotechnical and environmental engineering, with specialization in hydrogeologic site investigation. He is a former Instructor of Groundwater Hydrology at the University of Houston, and has authored numerous technical articles regarding groundwater remediation technologies. Mr. Connor served as co-principal investigator for the prior laboratory research on the in-situ radionuclide treatment process, and directed development of the associated U.S. Patent. ***Groundwater Services, Inc., 5252 Westchester, Suite 270, Houston, Texas 77005. Tel: (713) 663-6600. Fax: (713) 663-6546***

- **Dr. Dennis Clifford, Ph.D., P.E.** Dr. Clifford has earned B.S. and M.S. degrees in Chemical Engineering and a Ph.D. in Environmental Engineering from the University of Michigan. As a Professor of Environmental Engineering at UH, he teaches courses in water and wastewater treatment, water chemistry, and physiochemical treatment processes. Dr. Clifford has directed approximately $3 million of prior research into the removal of inorganic and radioactive contaminants from water and soil, and has more than sixty publications, including journal articles, book chapters, and refereed government reports. Currently, Dr. Clifford is North American Editor of the Elsevier Journal *Reactive Polymers*, which deals with the preparation and application of functional polymers (adsorbents, ion exchangers, and immobilized chelants) for separation processes. ***University of Houston, Dept. of Civil and Environmental Engineering, 4800 Calhoun, Houston, Texas 77204-4791. Tel: (713) 743-4266. Fax: (713) 743-4260.***

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Table 1
APPLICATIONS OF IN-SITU NORM REMOVAL METHOD

Stratigraphic Horizon	Reservoir Fluid Properties	NORM Treatment Application	Sorbent Placement Method
Unsaturated Soil Zone *(0-100 ft depth)*	Capillary pore fluid: • Ionic strength <0.01 M • Oxidizing environment • NORM concentration: 0-100 pCi/L	Permeable leachate barrier	In-situ precipitation
Shallow Aquifer *(0-2000 ft depth)*	Fresh to saline water: • Ionic strength <0.01 M • Moderately oxidizing or reducing environment • NORM conc.:5-100 pCi/L	Drinking water treatment	In-situ precipitation
Deep Oil and Gas Reservoir *(>>2000 ft depth)*	Brine fluid: • Ionic strength >1.0 M • Highly reducing • NORM conc.: 10-1000 pCi/L	Produced water treatment	Direct injection of solid

Table 2
Summary of Radionuclide Test Results on Offshore Oil Platform Brines from Gulf of Mexico

Offshore Operators Committee Survey: 1990

Parameter	Mean Value (pCi/L)	Standard Deviation	Range of Measurements (pCi/L) Lower	Upper
Radium 226	262	156	4.1	584
Radium 228	277	146	18	586
Gross Alpha	442	919	0	4100
Gross Beta	127	254	0	1200

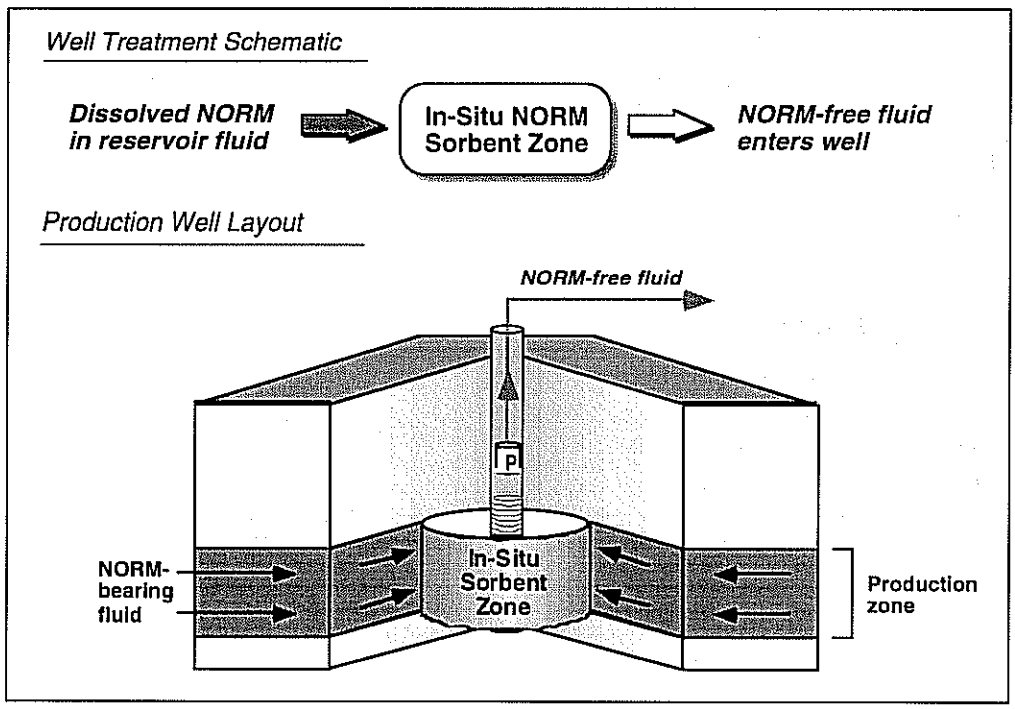

Figure 1. Overview of In-Situ NORM Removal Method

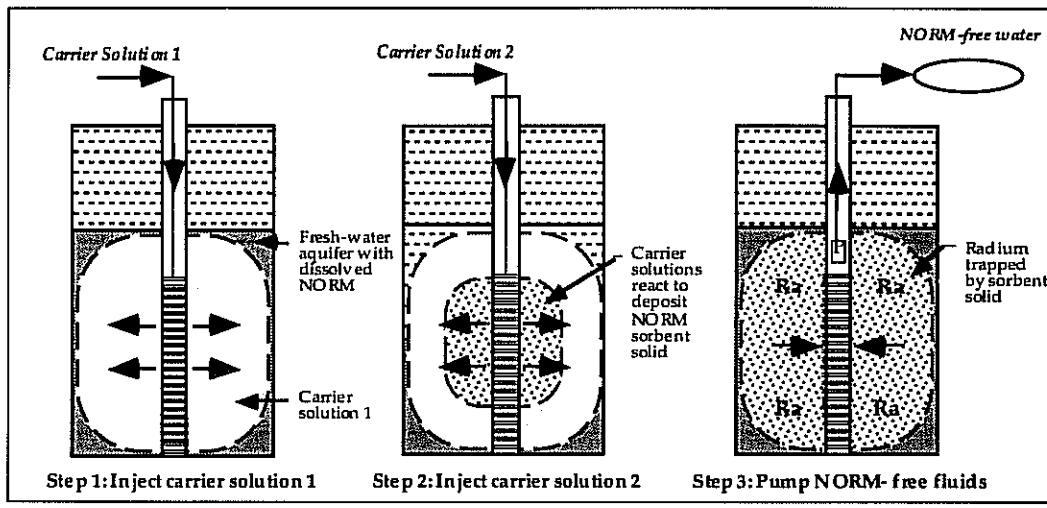

Figure 2. In-Situ Removal of Radioactive Materials from Water Supply Well

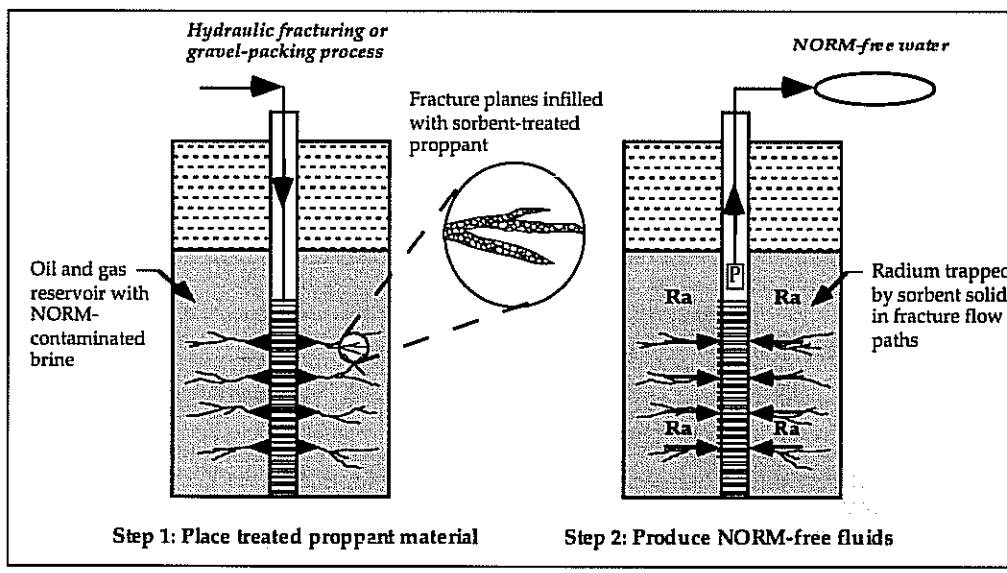

Figure 3. In-Situ Removal of Radioactive Materials from Produced Brine

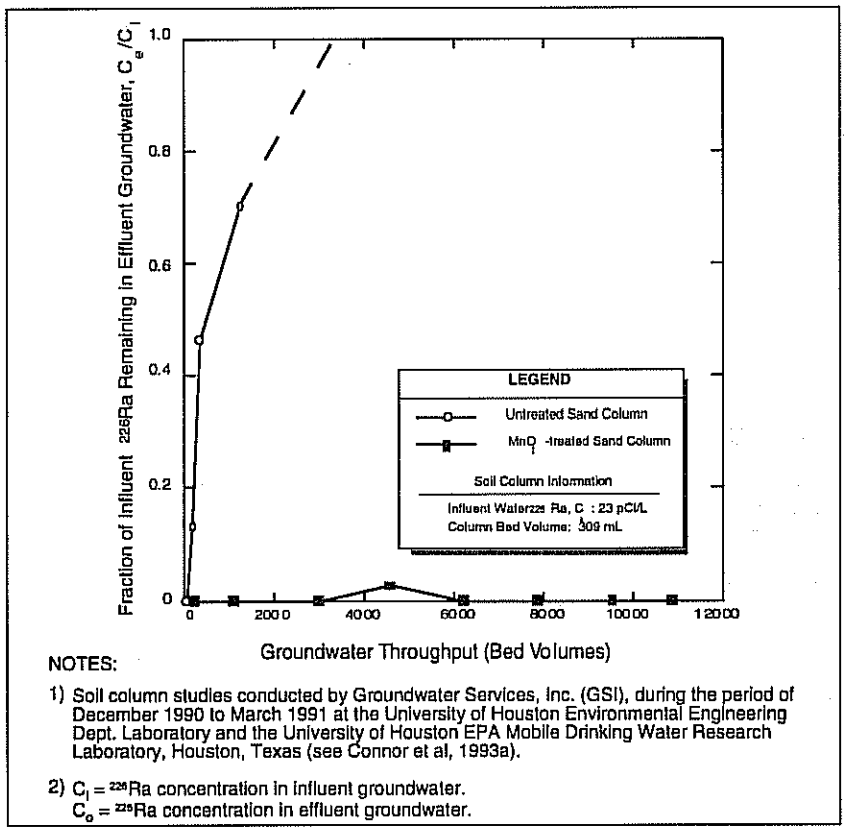

Figure 4. Performance of MnO_2 - Treated Sand in Removal of Dissolved ^{226}Ra from Groundwater

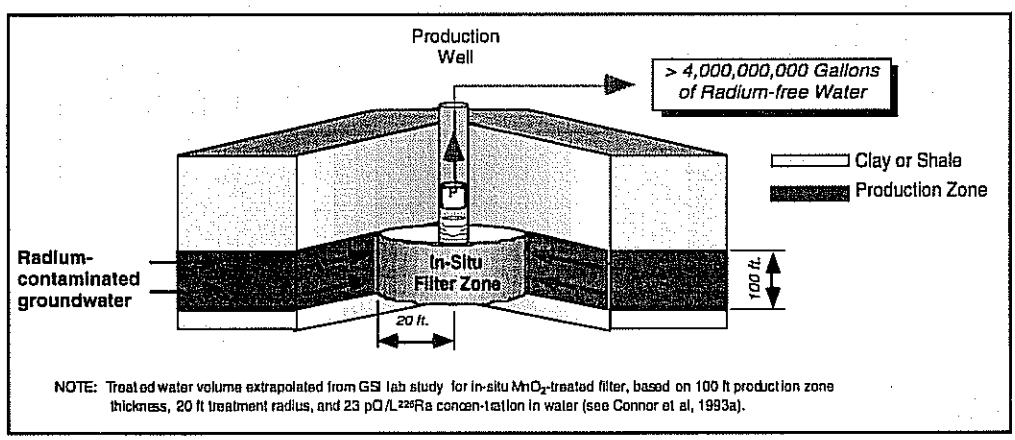

Figure 5. Performance of In-Situ Radionuclide Filter for Water Supply Well