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GARY D. CHESLEY

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DECONTAMINATION PERFORMANCE OF SELECTED *IN SITU* TECHNOLOGIES FOR JET FUEL CONTAMINATION

by

Gary D. Chesley

A major report submitted in partial
fulfillment of the requirements for
the degree of Master of Science
(Environmental Engineering)
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I. INTRODUCTION

Although jet fuels represent only about seven percent of the refinery production in the United States [Lander and Reif, 1986], incidents of significant jet fuel contamination have occurred. Such incidents include the 1975 leak of more than 314,189 liters near North Charleston, the early 1980s multimillion dollar decontamination effort near John F. Kennedy Airport, the spill at a U.S. Coast Guard Air Station near Traverse City, Michigan, and the 100,000 liter spill at Hill Air Force Base, Utah in 1985. Additionally, fuel spills are reported to account for nearly half of the chemically contaminated sites on U.S. Air Force installations [Downey and Elliott, 1990]. Decontamination of these sites is critical as more installations are announced for closure; each having to meet mandated environmental closure goals.

Specific study of jet fuel is warranted because of the quantitative and qualitative component differences between jet fuel and other hydrocarbon fuels. Quantitatively, jet fuel contains a larger aliphatic or saturate fraction and a smaller aromatic fraction than other fuels (i.e. heating oil and diesel oil) in the medium-boiling-point-distillate class of fuels [Song et al., 1990] as shown in table 1.1. Since the aliphatic and aromatic fractions of fuel are not equally susceptible to biodegradation [Gunnison, 1991], jet fuel decontamination using biodegradation may be different from other fuels.

Table 1.1 ANALYSIS OF FUEL COMPOSITION [Song et al., 1990]

Fuel Product	Class Composition (%)			
	Saturates	Aromatics	Polar	Carbon Range
Gasoline	not analyzed			$C_6 - C_{11}$
Jet Fuel	83.0	15.7	1.3	$C_9 - C_{17}$
Heating Oil	62.5	32.9	1.9	$C_9 - C_{22}$
Diesel Oil	53.7	45.0	1.3	$C_9 - C_{23}$

Qualitatively, jet fuel is a complex, heterogenous mixture of organic compounds [Hughes et al., 1984], comprised of a wide range of constituents from low-molecular-weight to high-molecular-weight compounds [Aelion and Bradley, 1991]--a much wider range than gasoline [Downey and Elliott, 1990]. Although this makes jet fuel more complex, it may also mean that more than one decontamination technique may be required to adequately decontaminate the wide range of components in jet fuel.

The purpose of this report is to review the performance of several in situ technologies for the decontamination of jet fuel contaminated sites.

III. BIOREMEDIATION

3.1 Introduction

Bioremediation is the use of biological methods in engineered systems to degrade, detoxify and immobilize target contaminants [Hicks and Caplan, 1993]. The term may apply to solid-phase treatment using land treatment systems, slurry-phase treatment systems conducted either in-place or within impoundments, or in situ treatment systems [Ryan et al., 1991]. Bioremediation of jet fuel proceeds because many indigenous microorganisms have the ability to degrade nearly all of the hydrocarbons found in fuels under either aerobic, anaerobic or anoxic conditions [Aelion and Bradley, 1991]. The conversion process brought on by microbial metabolism breaks down the hydrocarbons to innocuous by-products such as CO_2 and CH_4 [Thomas and Ward, 1991]. *In situ* bioremediation, therefore, attempts to provide optimum conditions where these broad microorganism degradative capabilities can be focused on an organic pollutant.

3.2 Principles and Methods

A determination of bioremediation feasibility and the rate at which it may occur must include an assessment of several factors. These factors essentially effect the recalcitrance of the contaminant and may be categorized as microbiological and environmental rate-limiting factors [Autry and Ellis, 1992;

McCarty, 1991].

The principle microbiological rate-limiting factor is the presence of a hydrocarbon degrading microbial population. However, these bacterial species are ubiquitous in nature and it is highly unlikely that any soil system would be deficient in such microorganisms [Autry and Ellis, 1992]. Possibly more rate-limiting are some aspects of the total microbial ecology at the site. Competition will exist between hydrocarbon degrading and non-hydrocarbon degrading populations for available nutrients, water, and energy sources. Additionally, natural bacterial predators, such as protozoa, may feed on the desired hydrocarbon degraders [Autry and Ellis, 1992].

Although little can be done concerning bacterial predation, competition among species for necessary carbon, water and energy sources may be reduced by manipulating several environmental rate-limiting factors. Successful optimization of the factors will allow the desired contaminant degraders to become the dominant population. These factors include a food and energy source, metabolic nutrients, an electron acceptor, water, favorable pH and temperature, and adequate contact and time.

In one case, the contaminant may serve as the carbon and energy source. In a second case, called co-metabolism, another organic may serve as the primary source and the contaminant is transformed to a non-toxic end product without significantly contributing to microbial growth [Ryan et al., 1991]. The cometabolic transformation is brought about by enzymes or cofactors produced by the microorganisms for other purposes. They may initiate the degradation of a wide range of compounds under aerobic conditions. Some of these compounds are the aromatics and aliphatics [McCarty, 1991] which comprise the bulk of jet fuel.

Beyond these microbial rate-limiting factors are environmental rate limiting conditions. Appropriate conditions such as an adequate electron acceptor are required regardless of the degradation environment--aerobic, anaerobic or anoxic. In aerobic environments, oxygen is the electron acceptor. An increase in oxygen availability is often sought with methods such as air sparging, addition of pure oxygen, and the addition of hydrogen peroxide (H_2O_2). The low solubility of oxygen in water and its high chemical reactivity often limit the amount that can be provided for *in situ* bioremediation [Fiorenza et al., 1991]. Aerobic processes currently represent the most effective method of hydrocarbon degradation. This is mostly due to the greater energy yielding capacity of aerobic respiration as compared to anaerobic respiration [Autry and Ellis, 1992]. CO_2 and water typically result as metabolic end products [Hicks and Caplan, 1993]. Anaerobic degradation utilizes compounds other than oxygen as the electron acceptor--typically sulfate, carbon dioxide, or reduced organics. These degradation pathways may give rise to off-gases (CH_4 or H_2S) depending on the initial organic compounds present [Hicks and Caplan, 1993]. Nitrate is often the electron acceptor in anoxic environments [Parkin, 1991].

Metabolic nutrients such as nitrogen, phosphorus, and under anaerobic conditions, sulfur, are required to form cellular material for growth and reproduction [Ryan et al., 1991]. Certain other trace elements such as potassium, iron, molybdenum, zinc, copper cobalt, and other may also be required [Hicks and Caplan, 1993; Parkin, 1991]. Water is required to prevent cell desiccation and serve as a subsurface supporting environment where microorganisms produce the enzymes necessary for the degradation of organic contaminants [Hicks and Caplan, 1993].

While most indigenous hydrocarbon degraders can achieve target contaminant degradation at temperatures between 8 - 30°C [Hicks and Caplan, 1993], 27°C was found to be optimum when temperatures of 17, 27, and 37°C were maintained to degrade a jet fuel spill [Song et al., 1990]. Lower temperatures reduce reaction rates and therefore, require longer reaction times.

Optimum pH ranges have been cited at 6 - 8. Certain sites may exhibit increased acidity due to the production of organic acids, and may require the addition of alkalinity depending on the site's buffering capacity [Hicks and Caplan, 1993; Parkin, 1991]. However, this phenomenon is site specific and no generalization regarding JP-4 biodegradation is made here.

Adequate contact between hydrocarbon degraders, nutrients and the contaminant is important, especially for *in situ* technologies where control of this factor is often more difficult than in above-ground treatments. (Above ground treatment typically utilize suspended or attached/entrapped growth bioreactors where flow, mixing and distribution can be mechanically monitored and controlled.) Factors such as contaminant hydrophobicity, sorption onto the soil colloid, and volatilization may make the contaminant unavailable for significant contact with the degraders and nutrients [Autry and Ellis, 1992]. Sorption of jet fuel to the soil can be significant. It has been reported that up to 60 percent of a spill on medium- or fine-grained sand will exist in the adsorbed phase [Jasiulewicz and Hildebrandt, 1992] and up to 90 percent of subsurface fuel remained adsorbed in an unconsolidated coastal sand [Downey and Elliott, 1990].

The requirement for adequate contact time between degrader and contaminant is often a difficulty with *in situ* treatment. The potential exists for long detention times providing that the microbial media migration is limited.

3.3 Applications

Laboratory experiments have demonstrated bioremediation of jet fuel in a variety of soil types and under a variety of temperature and nutrient conditions with oxygen addition [Aelion and Bradley, 1990; Song and Bartha, 1990]. Song and co-workers concluded that of the three medium-boiling-point-distillates examined (jet fuel, heating oil, and diesel fuel), jet fuel was the least environmentally persistent (diesel oil > heating oil > jet fuel) [Song, et al., 1990]. However, pilot-scale and full-scale *in situ* bioremediation of jet fuel appears to have been comparatively more difficult. For example, experimenters with a 1984 pilot-scale test at Kelly Air Force Base (AFB), Texas encountered significant soil permeability problems [Downey and Elliott, 1990]. Injection wells were not capable of delivering the required amounts of hydrogen peroxide and nutrients. Delivery was hampered by limited soil permeability with the *in situ* silt and clay, and by precipitation of calcium phosphates which formed as nutrient phosphates reacted with calcium in the soil. This limitation reduced the delivery of oxygen and nutrients; consequently little biodegradation occurred.

JP-4 remediation efforts at another Air Force installation, Eglin AFB, Florida also met with *in situ* complicating factors. The 12 meter thick unconsolidated coastal sand, the high ground water levels (one meter below the surface) and the soil's high hydraulic conductivity (6 x 10^{-2} cm/s) were thought to be properties of an excellent site for enhanced biodegradation testing. However, the presence of 10 mg/L of iron threatened to reduce permeability and cause failure of the reinjection well system with iron fouling. (Iron fouling has also been reported by Fiorenza et al. [1991]). An aeration basin and settling tank were added to precipitate and remove iron prior to re-injection [Downey and Elliott, 1990].

Additionally, the oxygen being transferred to the soil via hydrogen peroxide was found to be deficient. Only about 16 percent of the potential oxygen supply was actually delivered to the contaminated soil. The majority of the oxygen was escaping as an off-gas through shallow infiltration galleries [Downey and Elliott, 1990]. Subsequent experiments determined that indigenous bacteria produced peroxidase enzymes causing the rapid decomposition of H_2O_2 [Spain et al;, 1989]. Finally, even after a significant reduction of ground water aromatics at the site (8 ppm to 20 ppb), soil-bound fuel residuals remained above and below the water table [Hinchee et al., 1989].

Downey concluded that enhanced biodegradation success was unlikely at sites with low permeability and that even at sites with more permeable, sandy soils, fuel may be trapped within soil micropores and largely inaccessible to supplied nutrients and oxygen [Downey and Elliott, 1990].

III. VOLATILIZATION (SOIL VENTING)

3.1 Introduction

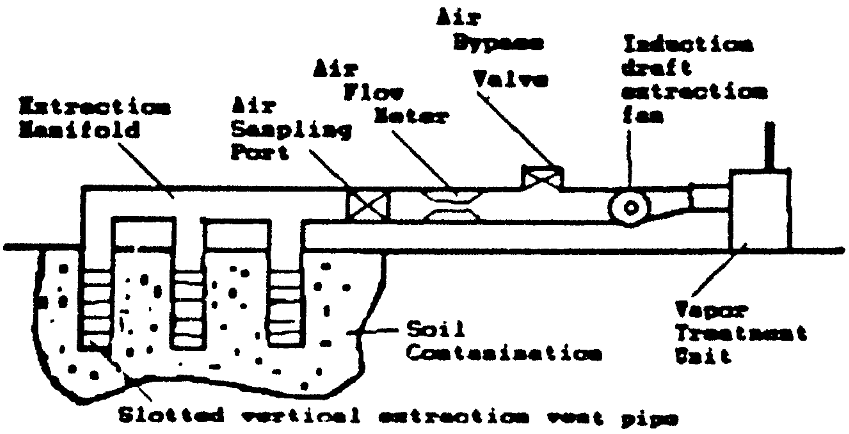
Volatilization, often called soil venting or vacuum extraction, was one of the most popular innovative technologies used for hazardous waste spill sites from 1988 to 1990 [Heller, 1992]. It is designed to remediate residual contamination in unsaturated soils (vadose zone) with high permeability. The process removes volatile organic compounds by creating air flows through contaminated soil. Vacuum blowers create the air flow, sweeping out soil gas, and disrupting the equilibrium between the contaminants on the soil and in the soil vapor. The contaminant is volatilized and carried out by the air stream [Connor, 1988; Downey and Elliott, 1990].

3.2 Principles and Methods

Soil venting system efficiencies depend on (1) vapor flow rate, (2) vapor flow path relative to the contaminant, and (3) the composition of the contaminant. As the vacuum well or vents create vapor flow through the soil, natural volatilization is increased. The higher vapor pressure components are volatilized first leaving the less volatile components in the soil [Johnson et al., 1990]. For example, the monoaromatic BTEX (benzene, toluene, ethylbenzene and xylene) hydrocarbons found in significant concentrations in gasoline would be expected to volatilize in the order of decreasing volatilities (benzene → toluene → xylenes → ethylbenzene) [Weast, 1971]. In this way, the concentration of contaminants in the vapor and their mass removal would be expected to decrease with time. (The JP-4 component naphthalene is even less volatile than the BTEX compounds.) [Newton, 1990].

Vapor flow paths in relatively dry, permeable soil enhance volatilization the greatest. However, if incoming air has a low relative humidity, the evaporative soil moisture loss could be significant enough to hinder microbial activity in the vadose zone [Johnson et al., 1990]. This is especially important if engineers are anticipating additional decontamination from biodegradation. Figure 3.1 depicts a typical volatilization system.

FIGURE 3.1: VOLATILIZATION SYSTEM



A vapor treatment unit may be required to treat the off-gas to acceptable limits. In this case, the upper portions of wells or trenches would be sealed to prevent loss of contaminated gas through short-circuiting [Connor, 1988; Newton, 1990].

In some gasoline recovery systems, the contaminated stream is passed through an activated carbon bed to adsorb the volatile organics. Later, the carbon bed is charged with steam and the vapor is sent to a condenser for cooling and separation of the water and gasoline liquids [Connor, 1988].

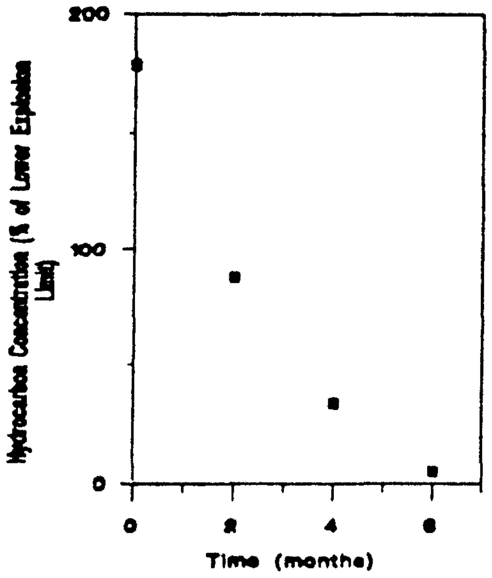
In situ volatilization has reportedly been successful at remediating many sites [Newton, 1990] including those contaminated with gasoline and trichloroethylene [Downey and Elliott, 1990]. However, JP-4 has more heavy molecular weight hydrocarbons and is less volatile than gasoline. [Downey and Elliott, 1990]. Therefore, it is not surprising that less data appears to exist for JP-4 volatilization efforts than for other, more volatile contaminants.

A number of *in situ* variables impact the degree of volatilization success. For example, increased soil water content decreases the rate of volatilization by reducing the soil vapor spaces that are available. Therefore, soil venting is often hindered if the vent wells or trenches are near groundwater. Increased soil porosity and permeability increase the amount of vapor that may travel through it. Soils with high clay contents tend to have low soil permeabilities and will have a large amount of the contaminant sorbed to the soil. Desorbtion must occur before volatilization is possible [Newton, 1990].

3.3 Applications

Successful JP-4 soil venting was demonstrated at Hill AFB, Utah at a spill site beginning in 1988 [Downey and Elliott, 1990]. The 100,000 liter spill had occurred nearly four years earlier in a medium to fine dry sand with interbedded layers of silty clay. The full-scale venting system design actually consisted of three subsystems. The first was a vertical vent array consisting of 15 vents to a 15 meter depth in the 37 by 37 meter contaminated area. The second was a lateral vent system consisting of six lateral vents at a 6 meter depth under a new concrete pad for the excavated underground storage tanks. The third was another lateral vent system, but located in the soil pile created by excavation of the underground storage tanks. Eight vents were located 1.5 meters below the top of the pile. The total system also included a blower, emissions control system, condensation drum, flowmeters, and gas monitors.

FIGURE 3.2: Soil Gas Hydrocarbon Concentration from JP-4 Soil Venting System [Downey and Elliott, 1990]



System performance has been measured by several parameters. Figure 3.2 indicates the declining trend in the soil gas hydrocarbon concentrations from an area of the vertical vent system. Concentrations were measured as a percent of the lower explosion limit (LEL).

Additionally, the hydrocarbon concentration in the extracted gas from the entire system was monitored. It reduced from a peak value in December 1988 of 38,000 ppm hexane equivalent to 50 ppm hexane equivalent in October 1989. This lowest value was reported to be below that required by some states (e.g. Florida) for mandatory site cleanup. Data from extracted gas samples have led engineers to estimate that 70 to 80 percent of the original 100,000 liter spill was removed by October 1989 [Downey and Elliott, 1990].

Engineers applying this technology should be aware of several application concerns. First, decreasing temperatures decrease the vapor pressure of a compound. A soil venting operation in cold air will increase the time required to achieve the same volatilization as in warmer air [Johnson et al., 1990]. Another rate related concern is that recovery rates will differ between a "fresh" spill and a "weathered" spill. Initially, the vapor concentrations for the fresh fuel will be greater because it would have contained greater amounts of the more volatile components. However, the weathered contaminant will experience less of a decline in recovery rates than the fresh spill. A third concern is that the vacuum created in the soil has the potential to cause an "upwelling" in the water table. The rise in water table can be significant, especially within five meters of the vacuum well. One model predicts a water table rise of up to three meters under typical conditions within a 2.5 meter radius of the vacuum well [Johnson et al., 1990]. If the soil contamination lies just above the water-table, such an upwelling could bring the water-table into the contamination zone, effectively contaminating more ground-water. A ground-water pumping well may be required in such a case.

IV. LEACHING (SOIL WASHING)

4.1 Introduction

Leaching or soil washing is a water-based decontamination process employed to wash contaminants from soil. It is essentially a method to reduce the volume of contaminated soil by concentrating the contaminant in a smaller soil fraction or by dissolving or suspending contaminants in the wash water [Duncan and Ngo, 1992].

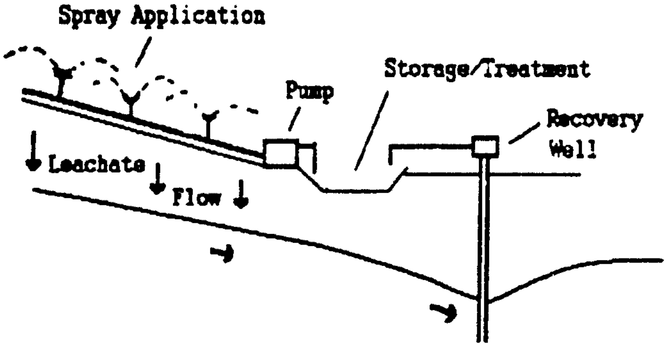
Soil washing has been common in the Netherlands and Germany and was used extensively to clean the well publicized, pesticide contamination along the Rhine River near Basel, Switzerland in 1986 [Duncan and Ngo, 1992]. However, its use in the U.S. is increasing. Soil washing technology was used at eight Superfund sites from 1986-89 [Stinson et al., 1992].

Although soil washing technology has been used often to treat excavated soil, it can be employed as an *in situ* technology where soil is not excavated. This approach has been used on at least one JP-4 contamination site [Downey and Elliott, 1990].

4.2 Principles and Methods

In situ leaching systems decontaminate the soil by passing a transport solution through the soil where it either reacts with the contaminant or is collected after passing through the soil. The transport solution may be introduced into the contaminated soil by injection piping, surface irrigation or infiltration ditches. Recovery of the wash water may be achieved with open ditches, porous drains or wells depending on specific site characteristics such as soil permeability and surface and groundwater flows [Newton, 1990]. Figure 4.1 depicts a typical leachate recycling system.

FIGURE 4.1: LEACHATE RECYCLING SYSTEM



The transport or wash solution is often a mixture containing a surfactant [Krukowski, 1993]. They are classified according to the nature of the hydrophilic portion of the molecule. Surfactants used to enhance soil washing efforts have included anionic, cationic, non-ionic, and amphoteric surfactants [Newton, 1990; West and Harwell, 1992]. The surfactant is required to reduce the interfacial tension between many petroleum constituents and the water. For instance, BTEX compounds are not highly soluble in water and only 20 to 30 percent of a spill can be found in the soil moisture or ground water [Newton, 1990]. Despite this low solubility of gasoline's BTEX compounds, gasoline is accessible to water-based treatment methods when using surfactants [Downey and Elliott, 1990].

Successful remediation is enhanced by matching the appropriate surfactant with the type of contaminant. One current attempt is called the Hydrophilic/Lipophilic Balance (HLB) method [West and Harwell, 1992]. The empirical HLB scale was developed for matching surfactant structure to an organic chemical to be emulsified in water. Each surfactant has an HLB number (which may be supplied by the manufacturer) that indicates the types of organic chemicals it can emulsify. The more water soluble the surfactant, the higher the HLB number. Organic chemicals have an HLB requirement. This requirement of an organic compound is related to the compound's hydrophobicity. The more water soluble the compound (less hydrophobic), the higher the HLB requirement. For example, dodecane (HLB=10) is less water soluble than dodecanol (HLB=14). Ideally, the appropriate surfactant may be chosen for a specific contaminant given the surfactant's HLB number and the contaminant's HLB requirement. However, this method still requires the incorporation of the quantitative impacts of temperature and electrolytes on surfactant performance.

Additionally, separation of the wash water from the surfactant and contaminants after wash water recovery has yet to be perfected. A number of technologies are under investigation and include foam fractionation, centrifugation, solvent extraction, surfactant hydrolysis, ultrafiltration, sorbent adsorption, ozonation, and ultraviolet treatment [Newton, 1990].

While not a truly *in situ* technology, many soil washing systems treat contaminated soil on site, but only after excavation. This technology is very popular, but is based on slightly different principles than the true *in situ* technology and therefore, deserves explanation.

These above ground systems operate on the principle that most contaminants tend to bind chemically or physically to the clay and silt portions of a soil matrix. These fractions provide a high surface area for binding, but contribute little to the total mass of a well-graded soil [Stinson et al., 1992]. Contaminant volume reduction is then achieved by physical soil particle size separation. This permits the bulk of the soil to remain on site for reuse provided that contamination in that soil fraction is within permissible limits. The highly contaminated, smaller soil volume may than be further treated. Because a relatively well graded soil is required, less than 25 percent should contain fines (silt and clay) [Stinson et al., 1992].

4.3 Applications

One of the major attractions for selection of a soil washing treatment is that it is one of the few processes that can remove heavy metals and semivolatile organics from the same waste stream. However, other contaminants (PAHs and naphthalene) have also been removed by soil washing in conjunction with other treatment technologies. A 1989 pilot-scale soil washing process demonstrated

83 and 88 percent removal efficiencies of PAHs during two tests at a Superfund site in Brighton, Minnesota [Stinson et al., 1992]. Such a process is currently underway at a Thunder Bay, Ontario site contaminated with 65,000 ppm PAH and 29,000 ppm naphthalene [Krukowski, 1993]. This decontamination capability is of interest as these components are also present in JP-4.

Because of these soil washing successes, and because of successful laboratory leaching of crude oils [Downey and Elliott, 1990], an attempt at in *situ* soil washing of a jet fuel contaminated site was arranged at a Wisconsin Air National Guard installation [Downey and Elliott, 1990]. Approximately 200,000 liters of JP-4, waste oils, and solvents may have contaminated the site since its first use in 1955 as a fire training area.

The soil consisted of 3 to 5 meters of an unconsolidated, uniform sand over a highly compacted sandstone. The relatively high soil permeability (4×10^{-3} to 5×10^{-3} cm/sec) made the site a candidate for soils leaching decontamination [Downey and Elliott, 1990].

Several 0.2 m^3, in *situ* test beds were established and determined to contain oil and grease contamination ranging from 1000 to 6000 mg/kg of soil. The test beds were then treated with 14 pore volumes of synthetic surfactant/clean groundwater solution at a rate of 70 liters/m^3/day. After six days of leaching, samples were collected from two depths in the test beds and revealed no significant reduction of oil or fuel contamination at either depth.

Experimenters cited differences between laboratory columns and in situ conditions such as soil density and permeability as possible reasons for the very different decontamination results [Downey and Elliott, 1990].

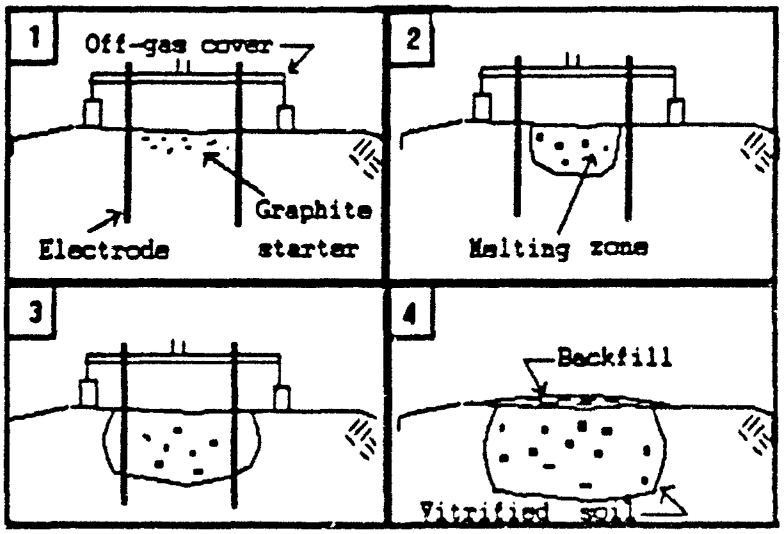
V. THERMAL TREATMENTS

5.1 Introduction

Two specific thermal technologies have been investigated for decontamination purposes--in *situ* vitrification and radio-frequency (RF) heating. *In situ* vitrification may not be a true "decontamination" technology as some of the contaminants are encapsulated and remain on site [Newton, 1990]. However, RF heating does volatilize hydrocarbons and allow them to be removed from the soil with off-gases [Downey and Elliott, 1990].

Figure 5.1 depicts the steps involved in the in situ vitrification process.

FIGURE 5.1: *IN SITU* VITRIFICATION PROCESS



5.2 Principles and Methods

In situ vitrification is a thermal treatment technology where electrical resistance heating converts contaminated soil into a solidified glass-like material. Electrodes of graphite or molybdenum are place in the soil and a mixture of flaked graphite and glass is place on the soil surface. This mixture assists electrical conductivity after soil moisture is driven off from heating. Temperatures in excess of 1900° F are required to melt the soil and sustain downward travel of the molten zone through the contamination. Organics are typically pyrolyzed in the melt and migrate to the surface where they combust in the presence of oxygen. Off-gases are collected with a hood and further treated. Inorganics are encapsulated in the solidified mass after cooling [Cudahy and Eicher, 1989; Johnson and Cosmos, 1989; Newton, 1990].

The advantage of in situ vitrification is that the process is relatively rapid and the solidified mass has a low leach rate. Additionally, the presence of extraneous materials does not generally cause significant operational problems, but treating high moisture soils will require more electrical power and a longer treatment period [Johnson and Cosmos, 1989].

RF heating utilizes electromagnetic wave energy in the range of 2 to 45 megahertz to heat soil. Volatile organic compounds are removed from the soil primarily by vaporization, distillation, and steam stripping [Johnson and Cosmos, 1989]. RF heating is a relatively low temperature thermal treatment and capitalizes on the low boiling point of jet fuel (as low as 150°F) [Downey and Elliott, 1990; Lander and Reif, 1986] to remove fuel components.

5.3 Applications

Although no cases of JP-4 decontamination using in situ vitrification have been discussed here, such a use is possible. Several vitrification projects have been used for decontamination of other hydrocarbon contaminants. Full-scale in situ vitrification processes using 3,000 to 4,160 volt power sources have achieved vitrification depths of 44 feet [Johnson and Cosmos, 1989].

RF heating technology was first developed for the petroleum industry to recover oil from oil shale and tar sands in the 1970s. Field tests confirmed the feasibility of heating geologic formations to 400°C. More recent laboratory experiments successfully decontaminated fuel and solvent contaminated soils at temperatures from 100°C to 150°C [Downey and Elliott, 1990].

A pilot scale test of this technology on a jet fuel, waste oil, and solvent contamination site was also successful. (Reference section 4.3 for a more complete contamination description). A test area 4 meters long, 2 meters wide, and 2 meters deep was heated by 39 electrodes. A vacuum and vapor barrier, placed over the heated area, collected the escaping soil gas. A target temperature of 150°C was achieved, then maintained for 4 days resulting in 97 percent removal of semivolatile hydrocarbons and a 99 percent removal of volatile aromatics and aliphatics. The entire RF process consumed about 800 kw-hr/yd^3 [Downey and Elliott, 1990].

VI. PASSIVE REMEDIATION

6.1 Introduction

Passive remediation is also an alternative at some contamination sites, and will often times be the least cost alternative. This does not imply that no engineering effort is required. Passive remediation often requires contaminant monitoring. In many cases, states require monitoring wells both upgradient and downgradient. However, passive remediation as the sole source of treatment is prohibited in some states if significant contamination exists [Newton, 1990].

6.2 Principles and Methods

Ironically, passive remediation may be most appropriate in areas of high contamination providing that the risk associated with not employing an active type treatment is acceptable. Anaerobic environments normally exist when contamination is high and anaerobic biodegradation of aromatic hydrocarbons has been shown to occur naturally in the environment [McCarty, 1991].

Aerobic biodegradation and volatilization may also occur naturally to decontaminate the soil. Indeed, unenhanced biodegradation of jet fuel has been demonstrated to occur in laboratory "untreated" samples where the resulting decontamination was greater than poisoned controls [Song et al., 1990], and in field sites [Rifai, 1988]. Additionally, passive biodegradation rates may increase over time as indigenous microorganisms adapt to degrade various organic compounds [Aelion and Bradley, 1990]. This is very possible in the case of JP-4 because it is such a complex mixture of many compounds [Aelion and Bradley, 1991; Lander and Reif, 1986] and because many JP-4 spill sites have gone untreated for several years [Aelion and Bradley, 1991; Aggarwal and Hinchee, 1991; Downey and Elliott, 1990; Hutchins et al., 1991].

The difficulty with passive remediation is in obtaining convincing evidence that natural decontamination processes are occurring, at what rates, and by what pathways [Madsen, 1991; McCarty, 1991]. A number of approaches to monitoring and verifying in situ hydrocarbon biodegradation have been utilized. They measure changes over time in hydrocarbon concentration, number of hydrocarbon-degrading microorganisms, oxygen consumption, or carbon dioxide production. Because of site variability and the difficulty in obtaining an accurate mass balance, these methods make it difficult to demonstrate definitive hydrocarbon biodegradation [Aggarwal and Hinchee, 1991]. One approach to verifying in situ hydrocarbon degradation is to measure stable carbon isotope ratios in soil gas CO_2 [Aggarwal and Hinchee, 1991]. The process is based on the principle that CO_2 produced by hydrocarbon degradation may be distinguished from that produced by other processes. The carbon isotopic compositions of the source material is differentiated from that accompanying microbial metabolism [McMahon et al., 1990; Suchomel et al., 1990].

Although passive remediation degradation rates may be slower, this may be the best overall engineering solution at appropriately contained sites as decontamination may still be achieved.

VII. DISCUSSION

7.1 Process Comparison

Engineers required to design a decontamination plan for a given site should be aware of the advantages, disadvantages, and applicability of each technology. Table 7.1 attempts to summarize the general applicability and requirements of each technology presented.

The obvious advantage of bioremediation is that it is an ultimate destruction technology [Autry and Ellis, 1992; Zitrides, 1990] which produces only innocuous end products and does not produce cross media contamination. Costs are moderate in comparison to other technologies because the required bacteria are ubiquitous and other rate-limiting factors are generally present in levels capable of sustaining biodegradation. With about twenty Superfund sites utilizing soil bioremediation in fiscal year 1989 alone, this technology has been described as cost effective and available [Ryan et al., 1991]. These factors combined with the idea that JP-4 hydrocarbons are generally well suited to biological treatment [Aelion and Bradley, 1991; Hutchins et al., 1991] make in situ bioremediation theoretically an excellent decontamination strategy for jet fuel.

However, some engineering difficulties have been encountered while implementing this technology for in situ JP-4 decontamination. The major challenge is the potential requirement for augmentation of an electron acceptor [Rifai, et al., 1988].

Table 7.1: **APPLICABILITY & REQUIREMENTS FOR SELECTED JP-4 DECONTAMINATION TECHNOLOGIES**

TECHNOLOGY	CONTAMINANTS REMOVED	ENHANCING ENVIRONMENTAL FACTORS	OTHER REQUIREMENTS	APPROXIMATE COST
Bioremediation	Soluble fraction[b]	High soil permeability[b] Most JP-4 in saturated zone[b] Shallow water table[b]	Addition of nutrients, e⁻ acceptor, microbes, pH control[b,c,e]	Moderate[l]
Volatilization (Soil Venting)	Volatile fraction[a]	Low soil moisture[a,l] High soil porosity and permeability[a,b] Low soil clay content[b,l] High temperatures/wind speed[l] Deep water table[j] Vadose zone decontamination[a,b,j]	Off-gas collection and treatment[j] Ground-water pumping well[d]	Low[l]
Leaching	Soluble fraction[j] Sorbed fraction[b]	Porous soils with high solubility, and low soil-water partitioning coefficient[i] Shallow water table[l]	Surfactants[j,k] Wash water separation[i] Clean Water Act permit[l]	Moderate[l]
Vitrification	Volatile/nonvolatile[f]	low soil moisture[g]	Significant electrical power[g] Off-gas treatment[f]	High[l]
RF Heating	Volatile organics[f]	low soil moisture[f,h]	Significant electrical power[f,g,h]	High[l]
Passive	Dependent upon the risk of contamination and extent of naturally occurring bioremediation / volatilization.		Acceptance by regulating authority[d,l] Monitoring[l]	Low[l]

[a] Johnson et al., 1990

[b] Fiorenza et al., 1991

[c] Parkin, 1991

[d] McCarty, 1991

[e] Hicks and Caplan, 1993

[f] Johnson and Cosmos, 1989

[g] "*In situ vitrification...*" <u>Process Engineering</u>, April 1987

[h] Downey and Elliott, 1990

[i] Stinson et al., 1992

[j] West and Harwell, 1992

[k] Johnson et al., 1990

[l] Newton, 1990

Delivery of this requirement may be difficult in low permeability silt and clay soils. Additionally, the use of H_2O_2 to deliver oxygen may be hindered as H_2O_2 could be rapidly decomposed by enzymes from indigenous bacteria [Downey and Elliott, 1990].

Volatilization or soil venting is a comparatively low cost option. The process is based on the existing chemical properties of JP-4 components and not on enhancement of biological reactions. And, although JP-4 typically has a lower bulk vapor pressure and is less volatile than gasoline, JP-4 has been demonstrated to be very accessible to air-based treatment [Downey and Elliott, 1990].

This technology is attractive if soil quality permits good fuel residual/transport media (air) contact and especially attractive if off-gas collection is not required, or requires only minimal tertiary treatment. However, if environmental regulations become based on total hydrocarbon concentrations, soil venting alone may not meet the mitigation goals rapidly enough [Johnson et al., 1990]. Biodegradation would then seem to be a logical follow-on treatment as the oxygen provided by venting may enhance the site's biodegradation potential.

In situ surfactant soils washing also depends primarily on contaminant physical properties and physical fuel/treatment fluid contact. However, most successful soil washing schemes have been conducted above ground and relied on additional technologies in a treatment train to achieve success. *In situ* JP-4 decontamination by soil washing was not found to be significant in the situations examined by Downey and Elliott [1990]. It should be generally true that leaching JP-4 would have less success than leaching gasoline since JP-4 has a smaller fraction of water soluble compounds [Downey and Elliott, 1990].

In addition to improving soil washing efficiency, surfactants complicate the use of this technology. The emphasis can no longer be placed strictly on the efficiency of surfactant solubilization. The engineer must also consider the fate of the surfactant because they may exhibit recalcitrance and/or toxicity in subsurface environments [West and Harwell, 1992].

The only RF heating, JP-4 decontamination pilot test examined in this report was highly successful in removing volatile JP-4 hydrocarbons. However, the direct energy costs were significant -- more than $75/yd^3 if current, domestic power costs were applied to the power consumption data [Downey and Elliott, 1990. The cost of RF heating would be expected to be greater than in situ vitrification as operating temperatures are achieved more quickly in the vitrification process. The requirement for off-gas capture and treatment remains for both processes.

With these engineering challenges and environmental limitations it is understandable why so many researchers and engineers caution against hasty efforts at full scale operations, but rather, recommend pilot studies and field tests first [Downey and Elliott, 1990; Hinchee et al., 1991; McCarty, 1991; Morgan and Watkinson, 1990; Ryan et al., 1991; Stinson et al., 1992].

Table 7.1 does include cost information in very general terms. Many of the factors discussed with each technology also impact costs. Therefore, a wide range of cost data exists in the literature and only some of the most general information was included in Table 7.1.

7.2 Combined Processes

Although each technology has thus far been addressed individually, more than one decontamination process may occur concomitantly [Aggarwal and Hinchee, 1991]. Some decontamination efforts have included attempts to separate and quantify simultaneous decontamination by biodegradation / volatilization [Aelion and Bradley, 1991; Song et al., 1990]. Other processes rely on the use of one process followed by another. All of the successful soil washing designs examined in this report relied on follow on processes, mostly biological, to achieve impressive removal efficiencies.

Future engineering emphasis appears to aim in the direction of combined technologies that utilize either concurrent decontamination or a treatment chain. Future projects are planned to investigate various technology combinations. One project will feature a soil venting/RF heating combination to more rapidly volatilize fuel residuals and increase volatilization of higher boiling point compounds. Another JP-4 project includes a soil venting process attempting to maximize biodegradation with vented air as the oxygen source, while minimizing volatile organic gas emissions. This process is sometimes called bioventing and it may be engineered in several configurations to maximize hydrocarbon reduction in the vadose zone [Fiorenza et al., 1991].

7.3 Future Challenges

Although experience and expertise with JP-4 decontamination technologies are growing, a number of challenges remain. One challenge with *in situ* bioremediation is to search for microbes and conditions that degrade more components of JP-4 more rapidly. Because JP-4 is composed of many compounds and because some evidence suggests that microbial degradation is compound specific [Aelion and Bradley, 1990], the potential for improvements in this area is vast. Investigations of this type may be hastened by the fact that the U.S. Air Force intends to implement some changes in the source and type of jet fuel used. These changes may impact decontamination technologies as the component quantities of JP-4 change.

First, alternate sources of jet fuel have been identified and are being studied for their potential in producing aviation gas turbine fuels [Lander and Reif, 1986]. The transition involves changing from light paraffin crude oils to heavier crudes (oil shale, tar sands, and heavy oils) as refinery feedstocks. Transition is required as light paraffin crude oils are diminishing and resources like oil shale are abundant world wide. The change in crude oil feedstock qualities has produced a new military jet fuel, JP-8X ["Jet fuel change over," 1988] and proposed a new "high density" fuel. This represents a change from the naphtha type JP-4 to a kerosene type jet fuel. Compared to standard JP-4, JP-8X and "high density" fuels are more dense, have a higher boiling point range, and have increased cycloparaffin content while decreasing aromatic content. The advantage of heavier fuels, beyond being produced from more readily available crude, is that they can have lower freezing points and will produce more energy per gallon resulting in greater aircraft range. The disadvantage from the decontamination perspective is that higher boiling points may reduce the applications of RF heating. More heat energy will have to be applied in RF heating to volatilize fuel residuals. New fuels may also impact in situ biodegradation technology applications. As jet fuels become more kerosene based and more dense, they may begin to approach to qualities of heating oils. In the area of biodegradation, heating oils have been shown to be more environmentally persistent than JP-4 [Song et al., 1990].

Whatever decisions are made by jet fuel producers and consumers, environmental engineers would be wise to monitor these decisions as they relate to current jet fuel decontamination technology.

CONCLUSION

Although jet fuel decontamination is achievable through several technologies, some engineering application challenges remain. They include oxygen delivery efficiency in bioremediation systems and optimum surfactant selection in soil washing systems. Combined processes are currently the subject of study and may assist engineers in reaching minimum contaminant levels at jet fuel spill sites. Finally, alternate jet fuel sources are driving a change in jet fuel components. These component changes may impact the choice of decontamination technology for implementation.

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