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Leaking Underground Storage Tanks:

Remediation with Emphasis on *In Situ* Biorestoration

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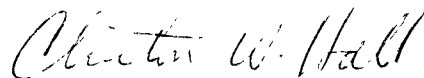
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Foreword

EPA is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise, and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the laboratory are responsible for management of research programs to: (1) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated zone and the saturated zone of the subsurface environment; (2) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (3) develop techniques for predicting the effect of pollutants on ground water, soil and indigenous organisms; and (4) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

This project was initiated to provide a state-of-knowledge document of remediation measures applicable to contamination resulting from leaking underground storage tanks. It has been estimated that more than three million underground storage tanks exist and 10 percent or more are leaking contaminants into the subsurface. The information found in this document includes sections on physical and hydrodynamic containment, withdrawal and treatment methods, in situ physical, chemical and biological treatment, hydrologic considerations and mathematical modeling of biorestoration, and institutional barriers to ground water pollution control. As the title indicates, emphasis is placed on biorestoration with topics including: (1) microbial activity in aquifers, (2) biostimulation by addition of limiting nutrients, (3) addition of specialized microbial populations to the subsurface, and (4) enrichment of specific microbial populations. This compilation will be useful to those having a need for information concerning possible remedial measures for ground waters contaminated by a variety of sources.

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Abstract

Leaking underground storage tanks have been identified as a major source of ground water contamination in the United States. More than three million underground storage tanks exist and 10 percent or more are leaking compounds such as gasoline, process chemicals, hazardous chemicals, and dilute wastes into the subsurface. As a result of the 1984 amendments to the Resource Conservation and Recovery Act (RCRA), regulation of underground storage tanks now applies to tanks which have at least 10 percent of their volume underground and which store petroleum products or hazardous liquid materials. Remedial techniques to restore contaminated aquifers have been developed because as many as 300,000 cases of leaks have been estimated in the United States. The state-of-the-art knowledge of measures available for remediation of contaminated ground water that results from such leaking underground storage tanks has been provided in this document. In situ biorestoration techniques are emphasized.

Treatment of contaminated aquifers has traditionally included physical containment, hydrodynamic control, and/ or withdrawal and treatment. In situ physical and chemical treatment schemes have also been developed.

The current literature indicates that in situ biorestoration has great potential for remediation of contaminated aquifers. In situ aquifer restoration involves the enhancement of the indigenous microflora to degrade subsurface pollutants. A second but unproven stategy is to add specialized bacteria to the subsurface. Aquifers amenable to biorestoration are usually those that are perfusable with solutions which carry the nutrients to the zone of contamination. The presence of indigenous microorganisms that can degrade subsurface contaminants has been demonstrated. However, a period of adaptation is usually required before the subsurface microflora can degrade the pollutants. Factors which may limit degradation, even in the presence of adapted organisms, include lack of an essential nutrient, substrate concentration, substrate inaccessibility, pH, temperature, and the presence of toxicants. Biorestoration of contaminated aquifers often involves the addition of limiting nutrients such as oxygen, nitrogen, and phosphorus. Enriching for microorganisms with special metabolic capabilities has been demonstated in the laboratory and may be promising in in situ biorestoration schemes. Mathematical models of biorestoration have been developed to simulate progress of the cleanup and provide information on the kinetics of the process.

Contents

List of Tables

List of Figures

I. Introduction

A. Importance of Ground Water Protection

Ground water is an important resource in the United States due to its current and expected increase in use as a water supply for domestic, industrial, and agricultural purposes. Two major issues of long-range concern include ground water depletion from over usage, and ground water quality impairment due to man-made pollution sources. Management of withdrawals to coincide with natural rates of recharge can minimize depletion concerns. Existing quality impairment can be alleviated by remediation techniques and preventative measures can be used to preclude further declines in the quality of the resource. Measures taken to prevent pollution of ground water are the best techniques for aquifer preservation.

One ground water pollution source category which has recently received increased attention is underground storage tanks, specifically, the inadvertent leakage of liquid products from such tanks into the unsaturated and saturated zones. This document was requested by the U. S. Environmental Protection Agency (EPA) Office of Underground Storage Tanks (OUST) to aid in planning a program for restoration of ground water contaminated by leaking underground storage tanks. The report is intended to be a state-of-the-art document to guide OUST in making judgements regarding the efficacy of alternative technologies for remedial action. The report specifically focuses on the use of innovative biological technologies to remove or attenuate contaminants.

B. Universal Impact of Leaking Underground Storage Tanks

One of the primary sources of ground water contamination has been identified as leaking underground tanks which store liquids such as gasoline, fuels, process chemicals, hazardous and toxic chemicals and dilute wastes (Cherimisinoff, Casana, and Ouellette, 1986). Snow (1985) has noted that of all the sources of ground water contamination, leaking underground storage tanks may pose the most serious threat to human health. The total number of underground storage tanks in the United States is probably upwards of three million. A conservative estimate is that 10 percent or more of these tanks are leaking, thus as many as 300,000 incidents of ground water contamination may be occurring (Dowd, 1984). Feliciano (1984) indicated that there are about 1.4 million underground tanks storing gasoline, with 85 percent made of steel and having no corrosion protection. The majority were buried more than 20 years ago. Some petroleum experts estimate that 75,000 to 100,000 of these tanks may be leaking their contents into ground water (Feliciano, 1984).

A national survey of underground motor fuel storage tanks has been conducted at 890 establishments covering 2,445 tanks (Klein, 1986). A subsample of 433 tanks was tested for leaks, with the following pertinent findings:

(1) An estimated 35 percent of the tank systems failed the tightness test. This conclusion must be interpreted with caution, however. In EPA's test, tank systems were filled above normal operating levels, which slightly elevated the normal operating pressure on the tank.

(2) The average rate for leaking tanks, adjusted for typical operating conditions, was 0.31 gallons per hour. Half the leaks were 0.25 gallons per hour or less. In the statistical analysis of this survey, EPA could not identify any variable (such as type of material or fuel type) that strongly correlated with test failure.

(3) At comparable ages, fiberglass and steel tanks showed no significant difference in the rate of test failure. Steel tanks comprise an estimated 89 percent of all underground motor fuel storage tanks, with fiberglass making up the rest. Steel tanks showed little increase in the rate of test failure with age in their first 20 years, but after 20 years failures increased.

(4) There are an estimated 796,000 individual motor fuel storage tanks, located at an estimated 326,000 establishments.

(5) The average age of tanks in the United States is 12 years.

(6) Twenty-one percent of the tanks are installed partially or completely below the water table.

1

In summary, underground storage tanks are ubiquitous and many are leaking. Existing tanks which are not currently leaking are expected to do so as they age. Therefore, there is a need for regulatory programs to protect ground water from this pollutant source.

C. Definition-Underground Storage Tanks (RCRA)

The Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act (RCRA) of 1984 (P.L. 98-616) added a new Subtitle I, "Regulation of Underground Storage Tanks". Part of these amendments require the EPA to develop and establish a national regulatory program for the control of new and existing underground storage tanks (U.S. EPA, 1985). The scope of this new program is broad and applies to tanks and combinations of tanks with 10 percent or more of their volume underground, including the volume of underground piping, that are used to store petroleum products or other liquid materials defined as hazardous substances under Section 101(14) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, commonly known as Superfund). The following tanks are excluded from the Interim Prohibition:

(1) farm or residential tanks having a capacity of 1,000 gallons or less for storing motor fuel for noncommercial purposes;
(2) tanks used for storing heating oil for consumptive use on the premises where stored;
(3) septic tanks;
(4) flow-through process tanks; and
(5) tanks above floor level but still underground.

Underground tank systems may leak due to several reasons. Corrosion, both external and internal, is considered the most common cause of leaks. Structural failure, primarily from improper tank installation, can also cause leaks. In addition, tank contents that are incompatible with a tank's liner and/or construction materials may induce leakage (Plehn, 1984). Poor operating practices have also been noted as a cause of tank leakage (Woods and Webster, 1984).

Existing tanks are to be addressed by an inventory and monitoring program. For example, among Subtitle I's provisions is the requirement that by May 8, 1986, underground tank owners notify designated state or local agencies of their tanks' existence. Under the law, EPA must also develop regulations for underground tanks addressing leak detection, corrective action, closure, record keeping and reporting, and new tank performance standards (Miller and Taylor, 1985). In addition, any new tank installed after May 7, 1985, must be designed, installed and operated so that it:

(1) will prevent releases due to corrosion or structural failure for the operational life of the tank;
(2) is cathodically protected against corrosion, constructed of noncorrosive material, steel clad with a noncorrosive material, or designed in a manner to prevent the release or threatened release of any stored substance; and
(3) the material used in the construction or lining of the tank is compatible with the substance to be stored.

In its interpretive rule, EPA has noted that the term "operational life" of a tank is "the time during which the tank stores regulated substances." The Interim Prohibition also has a limited exemption stating that a new tank does not have to be protected from corrosion if it is installed in a certain soil environment as follows:

> if soil tests conducted in accordance with ASTM Standard G57-78, or another standard approved by the Administrator, show that soil resistivity in an installation location is 12,000 ohm/cm or more (unless a more stringent standard is prescribed by the Administrator by rule), a storage tank without corrosion protection may be installed in that location.

Approximately one-half of the 50 states have initiated regulatory programs for underground storage tanks. In addition, local governmental agencies have developed regulatory programs (Zakheim and Ehrhardt, 1985).

2

D. Available Remedial Action Technology

Remedial action technologies for leaking underground storage tanks can be considered in relation to preventive measures and contaminant plume management. Preventive measures include corrosion prevention, proper installation practices, material, selection, and containment systems. Detailed information concerning preventive measures can be found elsewhere (National Technical Information Service, 1985; National Fire Protection Association, 1984; American Petroleum Institute, 1979; U. S. EPA, 1985). Plume management techniques may include one or several of the following (Repa and Doerr, 1986):

(1) ground water pumping to extract water from or inject water into wells to capture a plume or alter the direction of ground water movement;
(2) subsurface drains consisting of permeable barriers designed to intercept ground water systems;
(3) vertical underground barriers made of low-permeability materials to divert ground water flow or minimize leachate generation and plume movement; and
(4) innovative technologies that biologically or chemically remove or attenuate contaminants in the subsurface.

The most recent and innovative techniques for aquifer remediation involve stimulating the indigenous microflora to remove subsurface pollutants. Stimulation of the native microorganisms can result in the complete destruction of the contaminants whereas chemical or physical treatment may result in incomplete destruction or transfer of the contaminant to another phase of the environment. Biostimulation is often achieved by adding limiting nutrients such as oxygen, nitrogen, and phosphorus. The addition of specialized microbial populations to degrade subsurface pollutants has been incorporated into many remedial projects; however, their role in biodegradation could not be distinguished from that of the indigenous microflora.

E. Subsurface Effects on Contaminant Mobility

The transport and fate of products released to the subsurface environment from leaking underground storage tanks are dependent upon hydrodynamic, abiotic and biotic processes. A basic understanding of the nature and influences of these processes on contaminant mobility is necessary in the identification and implementation of appropriate remedial action technologies. The relative importance of the three basic processes is dependent upon both product (contaminant) characteristics and local hydrogeological features.

Some studies have been done on these processes as related to leaking underground storage tanks, and others are in progress. Biotic processes involving microbial degradation are obviously important for certain organic products, including many components of petroleum. For example, Jenson (1985) found positive evidence for natural biodegradation of gasoline which had leaked from an underground storage tank. In another example, ground water contamination was detected 30 m beneath a paint factory in Milan, Italy (Botta, Castellani, and Mantica, 1983). The pollution resulted from the leakage of organic solvents from underground storage tanks. Extraction of water samples at various pH values yielded three fractious: neutral, acidic, and basic. Aliphalic and aromatic acids were found in the acidic fraction, although their presence could not be attributed to industrial use. Observed concentrations of these and other compounds were attributed to oxidative microbial degradation of hydrocarbon components present in soil and ground water.

Hydrodynamic processes can also be involved in contaminant mobility. For example, the rate of movement of leaked oil into soil will depend on product viscosity and soil properties. Light products, such as gasoline, will penetrate rapidly, while heavy oils will move more slowly (American Petroleum Institute, 1980). The rate of penetration is also a function of the soil permeability. In clays with low permeability the product may penetrate very little, if at all; conversely, in sandy soil the penetration may be rapid. In the unsaturated zone, some oil may become trapped between individual soil particles, remain behind the main body of oil, and provide slow leakage of contaminants over a long period of time. This trapped or residual oil can remain in place for long periods of time. Residual hydrocarbons can occupy from 15 to 40 percent or more of the pore space as a result of these trapping processes depending on several physical characteristics of the subsurface. The ability to design and conduct successful remediation strategies depends largely on the ability to understand, predict and enhance the mobility of both liquid and dissolved hydrocarbons (Wilson and Conrad, 1984). Theoretically, there are a number

of ways the trapped residuals can be mobilized and concentrated such that a much lower content of residual product will have to be dealt with. Obviously, the most used mobilization technique is to increase the hydraulic gradient, usually by pumping, thereby increasing the Darcy velocity of the water phase in the saturated zone.

Light products can move to the surface of the water table in unconfined aquifers and spread out along this surface, occupying some of the capillary zone as well as the top layers in the water table (American Petroleum Institute, 1980). Finally, many oils and refined products contain components which are slightly soluble in water and other components which might volatilize. Solubility is greatest with lighter, aromatic components; these components are then influenced by advection and dispersion processes in the saturated zone. Soluble components can include benzene, toluene, and xylene. The mathematical modeling of multicomponent organic mixtures from leaking underground storage tanks is beyond the scope of this report; however, some work has been done in this area (Uchrin and Slater, 1985).

Abiotic processes can also influence contaminant mobility in the subsurface. These processes include adsorption, ion exchange, chemical precipitation and complexation. Adsorption of organics increases product retention, with the adsorption being a function of the octanol-water partition coefficient of the chemical and the inherent organic content of the subsurface media. Transport of metals from leaking underground storage tanks may be influenced by one or more of the above processes. The process that dominates depends upon the metal, soil characteristics, and subsurface environmental conditions such as pH and the oxidation-reduction potential.

II. Remedial/Restoration Plume Management Techniques

A. Physical Containment

Physical containment measures isolate contaminated soil and ground water from the local environment and minimize any threat to human health (Wright and Caretsky, 1981). Isolation techniques for the surface and subsurface include excavation and removal of the contaminated soil and ground water, barriers to ground water flow, and surface water controls. In a survey of 169 remedial actions by Neely et al. (1981), in situ containment and removal were the most frequently used options.

1. Removal

Excavation and removal of contaminated soil and ground water may be used when in situ containment or treatment is unacceptable (Wright and Coretsky, 1981). A pit is dug to remove the soil or pumping wells are installed to control the plume (Josephson, 1980). The excavated soil is transported to a secured site, such as a landfill or surface impoundment, for disposal (Ehrenfeld and Bass, 1984). The ground water is pumped out and can be treated using a variety of techniques. The cost of excavation of soil ranges from $1.75 to $4.50 per cubic yard. The inherent problem in excavation and removal to another location is that a new hazardous waste site is often created. Several Resource Conservation and Recovery Act (RCRA) facilities that have received contaminated materials from Superfund cleanups are leaking and are now new Superfund sites (Hileman, 1984). However, removal of contaminated soil and ground water to a more environmentally appropriate location may be necessary if in situ containment or treatment poses health risks or initiates litigation. Another problem associated with excavation and removal is that total removal of subsurface soil and ground water may be impossible when the contamination extends deep beneath the surface or the contaminants lay below an immobile facility.

2. Barriers to ground water flow

Physical barriers used to prevent the flow of ground water include slurry walls, grout curtains, sheet piling, block displacement and clay liners (Ehrenfeld and Bass, 1984). These impermeable barriers may contain contaminated

contaminated ground water or leachate or prevent the flow of clean ground water into a zone of contamination. Some general characteristics of slurry walls, grout curtains, sheet pilings and block displacement are compared in Table 2-1.

Table 2-1. Advantages and Disadvantages of Some Physical Barriers to Ground Water Flow (Hill et al., 1980; Canter and Knox, 1985; Brunsing and Cleary, 1983; Nielsen, 1983; Truett et al., 1982)

Methods	Advantages	Disadvantages

Slurry walls	very low upkeep
	fairly effective
	simple construction
	long service life
	minimal environmental
	  impact
		expensive
		bentonite deteriorates
		  in concentrated ionic
		  solutions
		must be anchored to
		  impermeable strata
		some construction
		  procedures patented
		bentonite availability
		  limited

Grout curtains	very low upkeep
	fairly effective
	increases soil's bearing
	  capacity
	long service life
	minimal environmental
	  impact
	used in consolidated and
	  unconsolidated material
	versatile
	specific targets can be
	  reached
	a variety of fluids can
	  be injected
		very expensive
		hard to place
		difficult to determine
		  completeness of wall
		some techniques are
		  proprietary
		limited to soils with
		  permeabilities of
		  10^{-5} cm/sec or
		  greater
		cannot be used at shallow
		  depths (1.5 m)
		some applications can
		  create additional
		  pollution

Sheet pilings	inexpensive for small
	  projects
	fairly effective
	minimal environmental
	  impact
	long service life
	sections of steel piling
	  are reusable
		difficult to form
		  effective barrier
		  in coarse, dense
		  material
		steel may corrode from
		  contamination
		not initially watertight

(Continued)

5

Table 2-1. (Continued)

Methods	Advantages	Disadvantages
Block displacement	economical when impermeable layer is deeper than zone of contamination isolates minimum amount of soil bottom barrier is formed without excavation	in developmental stages

Slurry Trench Cutoff Walls--

Aquifers with sandy surficial soil less than 60 ft in depth and underlain by an impermeable layer of fine grain deposits or bedrock are most amenable to slurry wall construction (Need and Costello, 1984). Construction of a slurry wall entails excavating a narrow trench (2 to 5 ft) surrounding the contaminated zone. The slurry acts to maintain the trench during excavation and is usually a mixture of soil or cement, bentonite, and water (Ehrenfeld and Bass, 1984). The trench is generally excavated through the aquifer and into the bedrock. Installation of a slurry wall at depths greater than 60 ft is difficult.

There are two different methods for construction of slurry walls (Tallard, 1984). Trenches constructed using a cement-bentonite (C-B) mixture are allowed to set whereas those constructed with a soil-bentonite (S-B) mixture are backfilled and solidified with appropriate materials. Solidification of the trench may be accomplished by backfilling with soil mixed with bentonite, soil mixed with cement, concrete, an asphaltic emulsion, or a combination of these with synthetic membranes (Lynch et al., 1984). The chosen materials should be compatible with the in situ soil and contaminant regime. Depending on the backfill material used, the permeability of the resulting barrier may range from 10^{-6} to 10^{-8} cm/sec (Nielson, 1983). A slurry wall isolation system may be constructed by placing a low permeability cap over a waste site that has been completely surrounded by a slurry wall (Need and Costello, 1984). Soil-bentonite trenches are commonly used in the United States (Tallard, 1984; Lynch et al., 1984). Further details on the construction, permeability, compressibility, and strength of a S-B wall in addition to the effects of pollutants on wall permeability are given in a paper by D'Appolonia (1980). Both S-B and C-B trenches are stable under normal conditions; however, C-B trenches deteriorate in the presence of acids and sulfates and S-B trenches are similarly affected by organics, calcium, magnesium, heavy metals, and concentrated ionic solutions (Canter and Knox, 1985). Laboratory tests should be conducted to determine the appropriate materials that should be used under the existing contaminant regime (Lynch et al., 1984; Tallard, 1984).

A S-B slurry cut-off wall was chosen for the first clean up financed by the Environmental Protection Agency's Superfund program (Ayres et al., 1983). The Gilson Road uncontrolled hazardous waste disposal site was an abandoned sand and gravel pit in which drums, chemical sludges, demolition debris, and municipal rubbish were illegally dumped. The underlying aquifer was found to contain a contaminant plume more than 1,500 feet in length, 110 ft in depth, with an areal extent of 30 acres. After removal of the drums, the site was filled, graded, and a S-B slurry wall isolation system installed. The design of the S-B backfill material is discussed in detail by Schulze et al. (1984). The cap was constructed with 40-mil high-density polyethylene (Ayres et al., 1983).

The use of synthetic liners in slurry trenches is an old concept but largely undemonstrated (Tallard, 1984). The problem with lining slurry walls is the difficulty in installation of the liner; the liner is usually welded at the

surface and placed in the trench with complex rigging. However, a liner can be custom designed to resist selected contaminants. One type of slurry wall liner system is constructed by backfilling a double liner sheet envelope with porous fill; observation wells are placed in the fill material to monitor seepage. The Envirowall vertical cutoff barrier is an example of such a hybrid cutoff wall (Arlotta et al., 1983). The trench is lined with high-density polyethylene (HDPE) and backfilled with sand; the permeability of the HDPE envelope is 10^{-12} cm/sec.

Slurry walls may also be constructed using the vibrating beam method (Canter and Knox, 1985). The vibrating beam wall is constructed by first excavating an 18-20 inch deep reservoir trench and then filling the trench with slurry (Schmednecht and Goldbach, 1984). An I-beam attached to a pressure hose is vibrated through the trench and into the ground. As the beam is withdrawn, slurry is injected into the ground under pressure. A vibratory driver-extractor became commercially available in the late 1950s that both drives and extracts the beam (Schmednecht and Goldbach, 1984). Slurries consisting of cement-bentonite or asphaltic emulsions may be used. Asphaltic emulsion cut off walls are more expensive but less permeable (1×10^{-8} cm/sec) and resistent to corrosive chemicals than C-B slurries. In comparison to S-B slurry walls, the vibrating beam wall may be more cost-effective because a smaller amount of grout is required to form the thin barrier (Tallard, 1984). However, heterogeneities in the subsurface soil or the vibrations from the injection process may result in a discontinuous wall; imperfections in the wall cannot be detected during the construction process.

Liners--

Liners, another type of physical barrier, are often used in conjunction with surface water controls and caps (Canter and Knox, 1985). In addition to use in slurry walls, liners may be used to protect ground water from leachate resulting from landfills containing hazardous materials. The type of liner used depends on the type of soil and contaminants which are present. The average cost of liner installation per acre is $40,000 to $50,000.

Liners include polyethylene, polyvinyl chloride (PVC), many asphalt-based materials, and soil-bentonite or cement mixtures (Canter and Knox, 1985). Polyvinyl chloride liners have permeabilities of less than 3.2×10^{-11} ft/sec; however, little is known about the service life of the PVC membranes (Threlfall and Dowiak, 1980). The membrane should be installed in fine-grained soil to prevent punctures.

Grout Curtains--

Grout curtains are another type of physical barrier which are constructed by injecting grout (liquid, slurry, or emulsion) under pressure into the ground through well points (Canter and Knox, 1985). Ground water flow is impeded by the grout that solidifies in the interstitial pore space. The curtain is made contiguous by injecting the grout into staggered well points that form a 2 or 3 row grid pattern (Ehrenfeld and Bass, 1984). Spacing of the well points for grout injection depends on the radial extent of grout penetration. In addition, the rate of injection is critical. Premature solidification occurs when the injection rate is too slow whereas the soil formation is fractured when the rate is too fast. Soil permeability is decreased and soil-bearing capacity is increased after the grout properly solidifies (Canter and Knox, 1985). Grouting is not effective in soils if 20 percent or more of the particles are less than 20 mesh in size. The average cost of grouting ranges from $142 to $357/ft^3.

Two types of grouting materials can be used: chemical and particulate grouts. Chemical grouts, consisting of two or more materials that gel upon contact (Canter and Knox, 1985) may be constructed with sodium silicate, phenoplasts, lignosulfonate derivitives, aminoplasts, or acrylamide (Ehrenfeld and Bass, 1984). The sodium silicate grout is the most widely used chemical grout, can be used at slow injection rates in fine sediments, is resistant to freezing and thawing, and reduces permeabilities from 10^{-2} to 10^{-8} cm/sec in sands. Phenoplasts and lignosulfates are rarely used because of problems with toxicity and high cost. Chemical grouts are not appropriate for acidic or basic soils and/or contaminants because the gelling process is an acid-base reaction.

Particulate, or suspension grouts, are a mixture of materials such as cement, bentonite, rock flour, clay, asphalt, or sand with water and are best suited for coarse or gravel soils (Canter and Knox, 1985). Suspension grouts made with Portland cement are widely used because they set within two hours (Nielsen, 1983). The composition of the

grout which is selected depends on the type of soil contaminants present. Of all the grouting techniques, particulate grouts are least expensive and most widely used.

Sheet Piling--

Construction of steel piling involves driving interlocking sections of steel sheet piling into the ground (Canter and Knox, 1985). The sheets are assembled before use by slotted or ball-and-socket type connections and are driven into the soil in sections. The piles are driven through the unsaturated zone, the aquifer, and down into the consolidated zone using a pile hammer (Nielsen, 1983). After driving the barrier into the consolidated material, the piles remaining above ground are usually cut off (Canter and Knox, 1985). The connections between the steel sheets are not initially water tight; however, fine grained soil particles eventually fill the gaps and the barrier generally becomes impermeable to ground water flow. Sheet piling may be ineffective in coarse, dense material because the interlocking web may be disrupted during construction (Nielsen, 1983).

Sheet piling is usually effective to depths of 49 ft; however, deeper barriers have been reported (Ehrenfeld and Bass, 1984). In addition to steel sheet piles, concrete also has been used. Concrete is expensive but is used when a barrier stronger than the steel sheet piles is necessary. Steel sheet piles are limited in that they may be susceptible to corrosion by some contaminants. The longevity of steel piling may be 40 years when the pH ranges from 5.8 to 7.8; however, a pH of 2.3 may limit the barrier to seven years of service. Construction of a 1700 ft-long by 60 ft-deep sheet pile was estimated to cost between $650,000 to $956,000 (Canter and Knox, 1985).

Block Displacement--

Block displacement is a method by which large areas of soil can be isolated by constructing an impermeable barrier around and underneath a block of earth (Cleary, 1980). The technique is currently under development for application to hazardous waste sites (Ehrenfeld and Bass, 1983). The bottom and surrounding barriers are constructed in two separate processes (Brunsing and Cleary, 1983). The bottom barrier is constructed by pumping a bentonite slurry into a series of injection wells. The subsurface material fractures as the slurry material from different wells coalesces. Continued pumping under pressure vertically displaces the block of earth. The amount of displacement corresponds to the thickness of the barrier. Construction of the surrounding barrier may be accomplished using traditional techniques such as slurry walls and grouting (Brunsing and Cleary, 1983). The surrounding barrier may be constructed first to induce a favorable stress field for formation of the bottom barrier (Ehrenfeld and Bass, 1984). The two barriers must intersect, regardless of which is constructed first. The type of slurry used for barrier construction depends on the same parameters considered for other types of physical barriers, i.e., soil type, ground water, and contaminant regime (Ehrenfeld and Bass, 1984). Block displacement may be preferable to slurry walls when the depth to the unconsolidated material is greater than 60 ft.

3. Surface Water Controls

Caps, dikes, terraces, channels, chutes, downpipes, grading, vegetation, seepage basins, and ditches are used to divert uncontaminated surface water away from waste sites and reduce the amount of infiltration and resulting hazardous leachate, or direct contaminated water away from clean areas (Ehrenfeld and Bass, 1984). Many of these techniques may be used in conjunction with each other. Surface capping usually involves covering the contaminated area with an impermeable material, regrading to minimize infiltration of surface water, and revegetation of the site (Canter and Knox, 1985). For example, the remedial action taken at an abandoned municipal/industrial dump that contained polychlorinated biphenyls (PCBs) included capping, revegetation, surface and subsurface drainage, and a gas control system (Blasland et al., 1982).

Surface caps are usually constructed using materials from one of three groups: 1) natural soils, 2) commercially-designed materials, or 3) waste materials (Canter and Knox, 1985). The material used should be compatible with the soil type and contaminant regime. Examples include clay, concrete, asphalt, lime, fly ash, and mixed layers of synthetic liners (Erdogan, 1984). Fine-textured soils, often from on-site, are most commonly used. The soil is compacted into a cap that covers the waste site and minimizes infiltration of surface water (Farb, 1978). Blending the soil with additives and cements may increase the effectiveness of the resulting cap (Canter and Knox, 1985).

8

Using a combination of different materials, such as loam, clay, and gravel, in layers may also improve surface water control. Commercially available materials such as bituminous or Portland cement concrete barriers and various types of membranes may be more desirable than soil when the waste is extremely hazardous. The average cost of cap installation ranges from $20,000 to $30,000/acre.

Dikes are used to control runoff or flood water whereas terraces are designed to divert surface water away from an area or control erosion (Ehrenfeld and Bass, 1984). Downdrain structures, such as chutes and pipes, are used to channel surface water downgradient (Doyle, 1980). Channels, or diversion ditches, are used to intercept runoff upstream of a location and direct the flow along a different course (Doyle, 1980). Surface water intercepted by channels may be diverted into seepage basins and ditches which discharge the water into the ground (Ehrenfeld and Bass, 1984). Grading changes the slope and runoff characteristics of a site; soil compaction is the most important method of grading. Revegetation may be appropriate after grading of a site to minimize erosion. Plants may also take up hazardous materials from contaminated soils in addition to aesthetically improving the appearance of the site. However, assimilation of hazardous materials by plants may pose environmental problems by providing an entry of the contaminants into the food chain.

There are no special limitations in using surface controls; however, surface controls only isolate the contamination rather than provide active treatment or management of plumes (Ehrenfeld and Bass, 1984). The availability of appropriate materials for surface caps may limit this approach. The use of other surface water controls depends on factors such as site topography, contaminant characteristics, and soil type.

B. Hydrodynamic Controls

Manipulation of the hydraulic gradient is one of the most commonly used methods for plume management and remedial action at hazardous waste sites. Shepard (1983) reported that hydrodynamic controls were required in most instances in which physical barriers such as slurry walls, grout curtains, and sheet piles were successful in plume management. Further analysis indicated that the hydrodynamic control would have been just as successful without the physical barrier.

The type of hydrodynamic control used may be passive or active. Passive hydrodynamic controls, or interceptor systems, function by gravity flow, whereas pumping is required for active control (Canter and Knox, 1985).

1. Passive Hydrodynamic Controls

An interceptor system is constructed by digging a trench below the water table; the process creates a zone of depression along the length of the trench (Canter and Knox, 1985). A perforated pipe is usually placed in the trench which is then backfilled with coarse material to aid in the collection and transport of water. There are two applications of interceptor systems, collector drains and interceptor trenches, which can be used as preventive or abatement measures. Collector drains such as leachate collection systems, are preventive measures against ground water contamination, whereas relief and interceptor drains are used to abate existing contamination. Relief drains are used in formations with relatively flat hydraulic gradients to lower the level of the water table or prevent contaminants from moving into deeper aquifers. Interceptor drains may be used to divert water away from a waste site or prevent contaminated water from entering an uncontaminated area. The second type of interceptor system, interceptor trenches, may operate by gravity flow or by pumping. The gravity flow, or passive interceptor trenches, are mainly used to remove pollutants such as hydrocarbons that float on top of the water table. The trenches remain open so that the contaminants can be removed with a skimming pump. The contaminants must be removed continuously to prevent seepage into the trench wall and transport downgradient in the formation.

The obvious advantage to using passive hydrodynamic control is the low cost of operation (Canter and Knox, 1985). Construction is simple, flexible, and the resulting system is reliable. However, passive control is not amenable to low permeable soils and deep aquifers, and usually cannot be installed underneath existing pits or other facilities. In addition, passive interceptor systems require frequent monitoring and maintenance.

2. Well Systems

Well systems are active measures of hydrodynamic control that rely on pumps or other mechanical devices for plume management. Active hydrodynamic control is the most frequently used technique for aquifer restoration (Jackson, 1982). The hydraulic gradient is controlled using withdrawal and/or injection wells (Canter and Knox, 1985). There are two types of withdrawal methods, well point and deep well systems. Well point systems are used in shallow aquifers and are comprised of numerous closely spaced wells that are centrally pumped. Deep well systems are designed for deeper aquifers and differ from well point systems in that the deep wells are pumped individually. Pressure ridge systems involve injection of water to manage plumes. Injection of water into the aquifer causes an upconing of the original water table which prevents the flow of ground water in that area.

Design of any well system must be preceded by a thorough hydrogeological characterization of the site (Canter and Knox, 1985; Nielsen, 1983). The number and placement of wells depends on the plume dimensions, hydraulic gradient, and the hydrogeological characteristics of the aquifer. Plume management may be accomplished using both withdrawal and injection wells (Nielsen, 1983). A row of withdrawal wells is placed upgradient while a row of injection wells is placed downgradient of a plume. The reverse hydraulic gradient either stops or reverses the flow of contaminated ground water between the rows of wells while uncontaminated ground water flows around the affected area.

Special types of well systems have been designed for hydrocarbon recovery because of economic considerations and the frequency of leaks from underground storage tanks (Canter and Knox, 1985). There are four such systems and they include systems with 1) one pump and one recovery well, 2) one pump with multiple wells, 3) two pumps and two recovery wells, and 4) two pumps and one recovery well. Each system takes advantage of the fact that hydrocarbons are relatively insoluble in water and float on top of the water table. Water-insoluble compounds other than hydrocarbons may also be recovered using these methods (Nyer, 1985). Systems utilizing only one pump produce an oil-water mixture which must be separated after recovery; however, the operation and cost of a single pump system is minimal in comparison to those with multiple pumps (Canter and Knox, 1985). A single pump system with multiple well points may be the system of choice in soils with low permeability.

Systems utilizing two pumps produce a separate oil and water phase (Canter and Knox, 1985). The system utilizes a shallow and a deep pump; the deep pump creates a cone of depression while the floating product is drawn to the center of the cone and recovered by the shallow pump. The shallow and deep pumps are housed in separate wells in the two pump-two well system whereas both pumps are housed in the same well in the two pump-one well system. The two pump-one well system requires a large well housing to accomodate two pumps, produces large quantitites of water, and requires continuous and careful monitoring during operation. The draw down pump of a typical two pump-one well system produces between 100 to more than 300 gallons per minute; the well casing is 26-inches in diameter and extends 35 ft below the water table (Peterec and Modesitt, 1986). Better separation of product and water is achieved when there is 30 feet between the depression and recovery pumps. The disadvantage of the two pump-two well system is the added cost and monitoring of a second well.

The two pump-one well system is the most commonly used. Smith (1986) described a recovery well system for an aquifer contaminated with hydrocarbons that consisted of five barrier wells located on the downgradient edge of the dissolved hydrocarbon plume and four product recovery wells (two pump-one well) positioned in the immediate spill area. The barrier wells removed the dissolved hydrocarbons that were not recovered by the recovery wells.

In lieu of two pump-one well systems which produce large quantities of water and are expensive to maintain and operate, Peterec and Modesitt (1986) demonstrated that 60 percent less water is produced and a more effective cone of depression can be achieved by pumping multiple shallow wells (4-inch diameter) at low flow rates. These small wells are fitted with pneumatically operated pumps which produce both hydrocarbon and water without generating an emulsion. In addition, the multiple well system reduces the exposure of uncontaminated areas that results from dynamic recovery operations using fewer wells. The use of observation wells as recovery wells also reduces the overall cost of the recovery operation.

Compounds such as the chlorinated hydrocarbons sink rather than float on top of the water table (Nyer, 1985). The contaminant must be located by sinking a well directly into the pool of material at the bottom of the aquifer. Because chlorinated hydrocarbons move in the same direction as the ground water (Keely et al., 1986), wells are used to force the material in the desired direction (Nyer, 1985). A one-pump system can be used which is controlled by a conductivity probe. The pump turns on when the pool of chlorinated hydrocarbon reaches the probe because electricity is not conducted by pure organic material.

The interceptor trenches described in Section B.1. under passive ground water controls may also be active (pumped). Active interceptor trenches contain vertical removal wells or a perforated, horizontal removal pipe and are usually backfilled with coarse material for stability (Canter and Knox, 1985). The system must be pumped continuously to remove the contaminants and prevent discharge downgradient of the trench.

There are many advantages of using well systems for aquifer restoration. Well systems are readily installed and existing monitoring wells are often incorporated into the design (Canter and Knox, 1985). The design of well systems is flexible and the cost for installation is often less than that of physical barriers. However, well systems are expensive and time consuming to operate and maintain. In addition, uncontaminated water is mixed with contaminated water during withdrawal which results in large volumes of water to be treated at the surface. Years of treatment may be required to successfully remediate a contaminated aquifer using well systems. Well systems may be minimally effective or not at all in low permeability formations.

C. Withdrawal and Treatment

Ground water can be treated using a variety of methods after withdrawal from a polluted aquifer. The treatment of choice depends on the nature of the contamination. Treatment of water contaminated with one compound may be simple, whereas spills of multiple compounds are complex and may require more than one treatment (Canter and Knox, 1985). There are numerous methods for physical, chemical and biological treatment of polluted ground water at the surface. These include biological treatment, carbon adsorption, catalysis, chemical oxidation, chemical reduction, chemical precipitation, crystallization, density separation, dialysis/electrodialysis, distillation, evaporation, filtration, flocculation, ion exchange, resin adsorption, reverse osmosis, solvent extraction, stripping, ultrafiltration, and wet oxidation (Ehrenfeld and Bass, 1984; Nyer, 1985). Processes most applicable to organic wastes include biological treatment, carbon adsorption, resin adsorption, chemical oxidation, stripping, reverse osmosis, sedimentation, flotation, and filtration. Many of the processes used have been borrowed from existing technology concerning water and wastewater treatment.

1. Chemical Treatment

Chemical treatments include such processes as neutralization, precipitation, oxidation-reduction, wet air oxidation, ozonation, addition of hydrogen peroxide, and coagulation (Ehrenfeld and Bass, 1984). Some general characteristics of selected chemical processes are given in Table 2-2. Water and wastewater have been treated extensively using precipitation and coagulation; however, these and other chemical processes are ineffective for removal of dissolved organic and inorganic materials (Sills et al., 1980). In addition, high concentrations of chemicals are necessary to treat heavily contaminated material and this produces a large volume of potentially hazardous sludge. Because of these drawbacks, chemical treatment is often used in conjunction with other processes.

Oxidation-Reduction--

Oxidation-reduction (redox) reactions may be used to remove some pollutants from ground water (Ehrenfeld and Bass, 1984). Redox reactions either raise or lower the oxidation state of a substance, thereby decreasing toxicity, solubility, or rendering the substance more amenable to removal. Currently, there are no demonstrated reduction reactions for organic compounds; however, many techniques are available for removal of organic compounds by oxidation.

The reduction of the toxic hexavalent chromium ion to the less harmful trivalent form is an example of a redox process. The process entails reduction of the hexavalent chromium ion by a reducing agent such as sulfur dioxide,

11

sodium bisulfite, waste pickling liquor from metal plating, or ferrous sulfate under acidic conditions (pH between 2 and 3). The pH of the solution is usually adjusted with sulfuric acid. The reduction of hexavalent chromium is rapid (5 to 15 minutes retention time). The resulting trivalent chromic sulfate is treated with alkali and then precipitated out of solution (Taylor and Qasim, 1983). The precipitate is removed by conventional solids removal techniques. Before the solution is acceptable for discharge, the pH must be readjusted to near neutrality (pH between 6 and 9) (Ehrenfeld and Bass, 1984). Before treatment, special precautions must be taken to remove any cyanide that may be present in the waste; adjustment of a waste containing cyanide to a pH of 2 to 3 may release hydrogen cyanide. Cyanide may be removed from a waste by chlorination (Ehrenfeld and Bass, 1984). Chlorination oxidizes the cyanide to nitrogen and bicarbonates and the treatment effectively removes cyanide to less than 1 ppm. The process involves adjusting the pH between 9 and 11 and adding chlorine gas or sodium hypochlorite.

Chlorine, hydrogen peroxide, and ozone are chemical oxidants that have been used widely in treatment of drinking water and industrial wastewater (Nyer, 1985). Ozone and hydrogen peroxide, but not chlorine, are also used in the treatment of polluted ground water. Chlorine is not used because the oxidation may form chlorinated compounds, such as chlorinated hydrocarbons, that are extremely undesirable in ground water.

Table 2-2. General Characteristics of Some Chemical Treatment Processes (Law Engineering, 1982)

Process	Removal Efficiency of Class I and II Compounds[a]	Capital and Operating Costs	Limitations
Ozone	Good removal of I and II	Moderate to high	Energy intensive
Hydrogen peroxide	Fair to incomplete removal of I and II with extended contact time	Modest capital and high operating	Incomplete oxidation of objectionable compounds
Coagulation	Poor removal of I and II	Moderate capital and high operating	No information
Resin Adsorption[b]	Good removal of some compounds in I	Moderate capital and high operating	No information
Ultraviolet radiation[b]	Good removal of I and II with extended time	Moderate to high	Expensive

[a] Class I compounds: xylenes, toluenes, benzene, ethyl benzene, and naphthalene
     Class II compounds: ether, alcohols
[b] Classified as both a chemical and physical treatment

As an oxidizing agent, hydrogen peroxide is stronger than molecular oxygen but weaker than ozone (Law Engineering, 1982). However, under alkaline conditions hydrogen peroxide may be a stronger oxidizer than ozone. Hydrogen peroxide can oxidize aromatic compounds with multiple rings and is readily available (Nyer, 1985). Drawbacks to use of hydrogen peroxide are numerous. Extended contact time for complete oxidation is required and the final result is often fair to incomplete contaminant removal. The high cost of this treatment limits its use to small operations (Nyer, 1985). In addition, hydrogen peroxide can impart an after taste in treated water (Law Engineering, 1982). Therefore, hydrogen peroxide treatment is often used in conjunction with processes such as ultraviolet radiation.

Ozone reacts with organic compounds to form less harmful, oxidized products (Ehrenfeld and Bass, 1984). The use of ozone is limited to dilute concentrations (<1%) of oxidizable compounds. Chlorinated hydrocarbons, alcohols, chlorinated aromatics, pesticides, and cyanides are susceptible to ozonation. Mixing and adequate contact time of the ozone with the contaminants is crucial because the rate of reaction is limited by mass transfer. There are numerous drawbacks to ozonation. Ozone is extremely reactive and special equipment that resists corrosion is required for the operation. In addition, ozone is acutely toxic and appropriate safety measures must be exercised. Like hydrogen peroxide, the process requires an extended contact time for efficient removal (Nyer, 1985). The capital and operating costs are moderate to high and therefore this technique may be of limited value in ground water contaminated with organic compounds (Law Engineering, 1982).

The removal efficiency of organic compounds using ozone may be enhanced by combining the treatment with ultraviolet (UV) radiation (Ehrenfeld and Bass, 1984). The reactor is equipped with UV lamps, positioned in the water at 3- to 6-inch intervals (Nyer, 1985). The UV light catalyzes the ozonation process. The UV-ozone process has been demonstrated to rapidly oxidize chlorinated hydrocarbons. Residence times of less than one minute were required to oxidize 100 ppb trichloroethylene to 0.6 ppb. Ultraviolet radiation may be used singly in treatment processes. Like hydrogen peroxide and ozone, UV light can be used to destroy organic compounds; in contrast, water treated by UV light has no odor or aftertaste (Law Engineering, 1982). However, an extended reaction time is required for good removal and the capital and operating costs are moderate to high. Therefore, UV light is generally used for small scale operations. Also, UV light cannot penetrate turbid or highly colored waters.

The Light Activated Reduction of Chemicals (LARC) process uses UV light in a reducing environment to dehalogenate various organic compounds (Kitchens et al., 1984). The photochemical reaction is conducted in a solvent, alcohol or water. The medium of choice radically affects the mechanism and efficiency of the process. Contaminated soil is extracted first and the resulting extract is then photochemically treated. Dehalo- genation of Arochlor 1260 extracted from soil followed pseudo-first-order kinetics (k = 0.052/min); total dehalogenation was achieved in 120 minutes. The dehalogenation kinetics of chlordane was pseudo-first-order (k = 0.029/min) and was complete in 180 minutes. Extraction and treatment of soils contaminated with 1500 mg PCB/kg using the LARC process is estimated to cost $84.60/ton of soil.

Neutralization--

Neutralization is another type of chemical treatment that is used to adjust the pH of the contaminated ground water (Ehrenfeld and Bass, 1984). The pH is usually adjusted between 6.0 and 9.0 using acidic or basic materials such as sulfuric acid, hydrochloric acid, and reagents containing sodium, calcium, or magnesium. Aqueous samples and a few nonaqueous materials are amenable to neutralization. Safety precautions and appropriate construction materials must be used because of the corrosive nature of acids and bases and care must be taken to ensure compatibility of the neutralizing agent and waste. Neutralization, however, does not remove the contaminant. The process is usually used in conjunction with other processes in a pre- or post-treatment scheme.

Precipitation--

Precipitation is a physical-chemical technique used to decrease the solubility of a particular contaminant by changing the chemical equilibrium of the waste (Ehrenfeld and Bass, 1984). The technique has been used routinely to remove inorganic compounds from wastewater (Canter and Knox, 1985). Precipitation may be

accomplished by adding a reagent that complexes the contaminant, adding a reagent that shifts the chemical equilibrium of the contaminant, or adjusting the temperature (Ehrenfeld and Bass, 1984). After precipitation, the insoluble material is removed using conventional methods for solids removal such as sedimentation, filtration, and centrifugation.

Materials used in precipitation processes include sodium hydroxide, sodium sulfide, calcium hydroxide, inorganic iron compounds, phosphate salts, and alum. Treatment with sulfide precipitates the most metals, but the resulting sludge may solubilize when exposed to oxygen (Canter and Knox, 1985). Oxidation of the sulfide complex to sulfate resolubilizes the metals. The carbonate process is difficult to control. The most widely used precipitation system employs hydroxides to remove metals; however, the resulting sludge may be viscous and difficult to dewater. The design for a precipitation system should consider the appropriate precipitating agent, dosage, time required for flocculation, and method for solids removal (Lee and Ward, 1986). The precipitation process can be limited by the presence of complexing compounds in the waste such as cyanide or EDTA; these compounds compete with the precipitant and keep the contaminant in solution (Ehrenfeld and Bass, 1984). Another limitation is that precipitation produces a sludge that may be hazardous and should be treated accordingly.

Coagulation--

Coagulation is another chemical process with origins in water and wastewater treatment technology. The process involves the aggregation of molecules of the contaminant to form a floc (Law Engineering, 1982). The floc is removed by conventional wastewater treatment techniques. The use of coagulation as a remedial treatment is limited because the process may not effectively remove low molecular weight organic compounds present in trace amounts. Coagulation is often used together with carbon adsorption for more effective removal of contaminants. In addition, treatment of high concen-
trations of waste by coagulation is not recommended because of the large volume of potentially hazardous sludge that is generated (Ghassemi et al., 1980).

Wet Air Oxidation--

Wet air oxidation (WAO) is a form of combustion that involves the addition of pressurized air to liquid wastes at high temperatures (Ehrenfeld and Bass, 1984). The process is suitable for the treatment of high concen-
trations of wastes with high removal efficiencies for low molecular weight organics and oily substances (Ghassemi et al., 1980). WAO requires highly skilled personnel, specialized construction materials, and cooling water.

2. Physical Treatment

Physical treatment methodologies include activated carbon adsorption, density separation, filtration, incineration, reverse osmosis, ion exchange, and air and steam stripping (Ehrenfeld and Bass, 1984).

Carbon Adsorption--

The most widely used treatment for liquid contaminants is activated carbon (Sills et al., 1980). Activated carbon is generally used to remove dissolved organic contaminants that are not removed by biological treatment. Some inorganic compounds such as antimony, arsenic, bismuth, chromium, tin, silver, mercury, and cobalt are partially removed (Ehrenfeld and Bass, 1984). The method is versatile because complex mixtures of organic compounds and volatile compounds can be treated (Hall and Mumford, 1985). The process involves passing an aqueous stream of waste through particles of granular activated carbon (GAC) or powdered activated carbon (PAC).

The contaminants are trapped and held on the carbon particles by physical processes (Nyer, 1985). The adsorbent nature of the carbon is a result of a high internal surface area which is independent of particle size. Granular carbon is widely used because it can be thermally regenerated, a process which also destroys the sorbed pollutants (Ehrenfeld and Bass, 1985). The carbon is usually thermally regenerated in a multiple hearth furnace but steam treatment, solvent extraction, and biological treatment are also used. Adsorption of organic material using

14

granular carbon employs moving or fixed bed reactors. Saturated adsorbent must be replaced or regenerated periodically. In contrast, powdered activated carbon is added to the aqueous waste and mixed for desired periods of time. After sufficient contact time, the powdered carbon is removed. The spent carbon is usually not regenerated. Powdered carbon may be used in the clarification step of biological treatment or added to aerated sludge. The spent particles settle out with the sludge in the latter application and may improve the settling properties of the sludge.

In conventional wastewater systems, carbon adsorption is generally used for wastes containing 1 percent or less adsorbable contaminants; however, the technique is often used for more concentrated wastes in remedial action (Ehrenfeld and Bass, 1984). The amount sorbed depends on the equilibrium of the solute between the carbon particles and solution (Canter and Knox, 1985). The affinity of the carbon for the organic substance depends on the 1) solubility of the organic compound, 2) solution pH, 3) molecular structure of the organic compound, 4) temperature, and 5) surface characteristics of the adsorbent.

Proper design of an activated carbon unit for treatment of contaminated ground water involves selection of carbon with appropriate physical properties and determining the carbon dosage and contact time required for efficient removal. Equilibrium adsorption isotherms are used to determine whether the contaminant can be effectively removed, the adsorption capacity of the carbon for the contaminant, and the amount of carbon required (Canter and Knox, 1985). Estimates of treatability can be made from the adsorption isotherms; however, column studies in the laboratory should be conducted to determine contact time, bed depth, pretreatment requirements, head loss characteristics, and carbon dosage (Canter and Knox, 1985). The breakthrough curve for the carbon column should also be determined (Ehrenfeld and Bass, 1984). An example of such a study was reported by Chrobak et al. (1985) in which pilot plant experiments were used to predict the performance of GAC adsorption in removal of chlorinated solvents.

Even with careful design based on good data, carbon adsorption is affected by fluctuation in flow rates and the composition of the waste (Ehrenfeld and Bass, 1984). Therefore, systems are generally designed to compensate for these variations. In addition, the carbon must be replaced or regenerated before binding sites are saturated and adsorption efficiency declines. Hall and Mumford (1985) reported that the life expectancy of the carbon bed is affected by the type and concentration of the pollutants, column size, and volume of water treated. Microbial growth may occur in the carbon system which may improve adsorption by removing contaminants or hinder the process with biofouling and/or production of objectional odors.

Granulated activated carbon (GAC) is well suited for treating ground water polluted with contaminants in the 500 ppb or less range (Stenzel and Gupta, 1983). Such conditions are often found in contaminated aquifers tapped for drinking water. GAC has been reported to remove contaminants in this concentration range to nondetectable levels. In addition, GAC is an excellent choice for remedial action of ground water contaminated with higher concentrations (ppm) of pollutants. Such contamination regimes may result from percolation of leachate from lagoons or waste sites into shallow aquifers. GAC may be the preferred treatment over air stripping in this case because stripping releases hazardous emissions and/or may not remove contaminants to acceptable levels.

Use of GAC in remedial action is cost-effective because of the regenerative capacity of the carbon (Stenzel and Gupta, 1983). The overall cost of treatment depends on flow rate, type and concentration of contaminants, and site requirements (Canter and Knox, 1985). Treatment of wastes in the ppm range may cost between $0.48 to $2.52/1000 gallons whereas $0.22 to $0.55/1000 gallons was reported for concentrations in the ppb range.

Resin Adsorption--

Resin adsorption is a physical-chemical process in which dissolved substances are removed from solution by synthetic or natural materials (Law Engineering, 1982). The resins may be ionic or nonionic; the nonionic materials form stronger bonds which are harder to reverse. Therefore, weak ionic or nonionic resins are more widely used. Synthetic resin adsorbs dissolved substances by trapping and holding the solutes in its molecular structure (Nielsen, 1983). In comparison to activated carbon, resin adsorption is more selective for some compounds; non-ionic resin polymers readily sorb low molecular weight lipophilic substances such as the alkyl

15

benzenes (Law Engineering, 1982). In addition, the rate of resin fouling is slower than that of carbon adsorbants. After saturating the binding sites, the resin can be regenerated chemically at relatively low cost (Nielsen, 1983). However, use of resin adsorption may be limited to small operations because of the moderate capital and high operating costs (Law Engineering, 1982).

Ion exchange--

Ion exchange is another type of adsorption process which has been demonstrated for removal of most inorganic dissolved salts, some organic dissolved salts, and some low molecular weight lipophilic compounds (Ehrenfeld and Bass, 1984; Law Engineering, 1982). In the past, this process has been used to remove unwanted ionic species from waste streams (Ehrenfeld and Bass, 1984); however, the use of weak ionic resins has generated interest in using the process to remove dissolved organic contaminants (Law Engineering, 1982). Ion exchange can be cost-effective because the treatment bed can be regenerated (Ehrenfeld and Bass, 1984). For regeneration to be practical, waste streams should contain 2500 mg of total dissolved solids/liter or less. Cost effectiveness is reduced and the application of ion exchange is limited for more concentrated wastes.

Stripping--

Stripping with air or steam is used to remove dissolved volatile organic compounds from wastewaters (Ehrenfeld and Bass, 1984). Air stripping involves transferring a dissolved substance from the liquid to the gas phase whereas steam stripping is essentially a distillation process in which the volatile pollutants are removed from the waste as the distillate. Removal of trihalomethane and trichlorethylene has been demonstrated for air stripping. Volatile organic compounds, ammonia, hydrogen sulfide, and water-insoluble compounds such as the chlorinated hydrocarbons, are amenable to steam stripping. High removal efficiencies using either air or steam stripping can be achieved. Removal of trichloroethylene from ground water by air stripping exceeded 99 percent whereas 10 to 99 percent of some volatile organic compounds was removed by steam stripping. The stripping potential of a particular compound can be predicted using Henry's Law constant (Canter and Knox, 1985). Compounds with high Henry's Law constants are more easily removed. The driving force of the removal is the concentration differential between the liquid and air phases; the rate of mass transfer is also important.

Air stripping can be accomplished using aeration tanks, cascade aerators, spray basins, or packed towers; the latter two methods are more economically and technically feasible (Nyer, 1985). The packed tower is the more commonly used method for remedial action on ground water because of the high interfacial area and high air-to-water volume ratios (Canter and Knox, 1985; Nyer, 1985). The system operates in a countercurrent fashion by which the aqueous waste flows downward through a tower of packing material while the air current is forced upward. The stripped water is collected at the bottom of the tower for proper disposal or treatment and the volatiles are emitted from the top with the air.

Factors that control stripping efficiency include tower height and diameter, the air-to-water ratio, and the temperature (Canter and Knox, 1985; Nyer, 1985). Elevated temperatures will increase the rate of stripping in addition to removing compounds that are not stripped at lower temperatures. Packed towers include an aeration system, devices to insure that mass transfer occurs optimally, and packing material in the tower shell. The packing material should create turbulence and provide a large surface area for air-water contact; corrosion resistance, weight, and cost of the packing material should also be considered. Polypropylene is often used as the packing material because the plastic is chemically inert, inexpensive, lightweight, and strong. Design of an air stripping tower should be preceded by pilot studies that incorporate site specific characteristics (Stover and Kincannon, 1983).

The obvious limitation in the use of air stripping is the release of hazardous pollutants into the atmosphere (Nyer, 1985). However, the pollutants that are released into the atmosphere are less concentrated than those in the wastewater because of dilution. In addition, some compounds such as tri- and tetrachloroethylene that are released in the atmosphere are subject to photolysis by the sun. Finally, hazardous emissions from stripping towers may be treated by activated carbon or incineration. A combination of air stripping with activated carbon may be less expensive than carbon treatment alone. Stripping towers are also subject to freezing, biofouling, and

16

clogging. Estimates for stripping trichloroethylene with a 90 percent efficiency ranged from $0.09 to $0.90/1000 gallons (Canter and Knox, 1985).

Incineration--

Incineration is a conventional and demonstrated technique used to destroy organic wastes (Ehrenfeld and Bass, 1984). The process theoretically involves the complete destruction of organic materials to inorganic species such as carbon dioxide, water, sulfur dioxide, oxides of nitrogen, and hydrochloric acid by raising the temperature of the waste in the presence of oxygen; temperatures ranging from 815 to 1094°C are employed for the oxidation (Nyer, 1985). Rotary kilns are most commonly used to incinerate mixtures of wastes with solid residues but multiple hearth, fluidized bed, and liquid injection incinerators are also available (Ehrenfeld and Bass, 1984). Multiple hearth incinerators accomodate liquids and gases in addition to solids and sludges, whereas liquid injection incineration is limited to liquids and slurries that can be pumped. The fluidized bed incinerator is suited for solids, liquids, and gases.

The suitability of a waste for incineration depends on multiple characteristics such as moisture content, volatile substances content, specific gravity, metal content, flammability, reactivity, and toxicity (Ehrenfeld and Bass, 1984). A self-sustained burn can be achieved with aqueous wastes containing 20 percent or more organic material; however less concentrated wastes will require auxiliary fuel (Nyer, 1985). Ground water is rarely polluted with 20 percent or more organic wastes.

A federally regulated incinerator must achieve an afterburner temperature of 1200°C and a two second dwell time and requires three percent excess oxygen (Ehrenfeld and Bass, 1984). Emission control equipment to remove sulfur dioxide, hydrochloric acid, and products of incomplete incineration should also be included when appropriate. Before a full scale incinerator is designed, pilot tests are conducted to determine the residence time, temperature, destruction efficiencies, ash residue, and gaseous effluent for a particular waste.

Incineration may be economically feasible for concentrated waste that can sustain a burn (Nyer, 1985). Incineration of small quantities of wastes may not be economically feasible unless the treatment facilities are nearby or mobile incineration units are available. Limitations other than cost include potential air pollution and the substantial upkeep that is required.

Design of a mobile incineration unit for the EPA was started in 1976 to provide a more cost-effective process (Freestone and Brugger, 1980). A rotary kiln design was chosen to accommodate a variety of organic wastes. A trial burn using the mobile unit was conducted and destruction efficiencies of ¡99.99 percent were reported for carbon tetrachloride, chlorinated benzenes, and Aroclor 1260 (PCB) at feed rates of 70, 95, and 50 lb/hr, respectively (Yezzi et al., 1984). The EPA has also been involved in the development and feasibility studies of another mobile incineration system, a High-Temperature Fluid-Wall (HTFW) reactor (Hornig, 1984). The removal efficiency for a 1 percent spike of Aroclor 1242 in soil was 99.9997 percent.

Reverse Osmosis--

Reverse osmosis (RO) is a filtration process by which inorganic salts and some organic substances (with molecular weights >300 g/mol) are removed from solution by passing aqueous wastes through a semi-permeable membrane under pressure (Ehrenfeld and Bass, 1984). The inorganic and some organic substances are concentrated on one side of the membrane while water passes through (Nyer, 1985). The osmotic pressure of the waste solution is counteracted by the applied pressure so that the solute can be concentrated (Ehrenfeld and Bass, 1984). Pressures between 200 to 400 psi are required.

The most commonly used membranes in RO include cellulose acetate, cellulose triacetate, polyamides, and polysulfones; however, many other membranes are in the developmental stages (Ehrenfeld and Bass, 1984). Cellulose acetate is most commonly used; however, the other membranes may be better suited for a particular waste depending on the pH, temperature, and nature of the contaminants. A polyether polysulfone membrane was reported to remove at least 90 percent of the benzene, hexane, and many chlorinated solvents in leachate at concentrations in the low to middle ppb range (Whittaker, 1984).

17

In general, removal efficiencies of total dissolved solids (up to 50,000 mg/L) from waste streams is greater than 90 percent (Ehrenfeld and Bass, 1984). Organic compounds of low molecular weight are not removed by RO (Nyer, 1985); the removal efficiency of organic compounds usually decreases with an increase in polarity and hydrogen bonding with the filter (Ghassemi et al., 1980). Removal efficiencies for oily substances and most heavy metals by RO are greater than 90 percent.

The limitations of wastewater treatment using RO are related to membrane fouling. The removal efficiency of the membrane can be compromised by suspended solids, biological growth, strong oxidizers, extremes in pH, and high concentrations of substances such as phenols, calcium, silica, sulfate, and aluminum (Ghassemi, et al., 1980). Pretreatment may be necessary when the waste stream characteristics are variable (Ehrenfeld and Bass, 1984). In addition, RO is expensive because of the high pressure required to drive the process (Nyer, 1985).

Density Separation--

Density separation encompasses the processes of sedimentation and dissolved air flotation (Ehrenfeld and Bass, 1984). Sedimentation involves the removal of suspended solids that settle out by gravity and is often used after chemical precipitation and biological treatment using activated sludge. The process can be enhanced by the addition of flocculants. Flocculation is a two-step process (Nyer, 1985). The first step is to neutralize the charge (usually negative) on the suspended particles so that flocculation can occur. Neutralization may be achieved using inorganic coagulants such as lime, alum, and ferric chloride. Other agents may be used when the treated water will be used for drinking water supplies. The second step in flocculation is to coalesce the smaller particles to produce larger particles, or flocs. High concentrations of small particles usually coalesce with gentle mixing. However, gentle mixing may not be sufficient to flocculate low concentrations of suspended particles. In this instance, special equipment and the addition of organic flocculating agents may be required. Sedimentation is attractive because of the low cost (Ehrenfeld and Bass, 1984).

Dissolved air flotation is used to remove insoluble particles of pollutants or nonaqueous phases of compounds such as hydrocarbons from waste mixtures (Ehrenfeld and Bass, 1984). The waste mixture is first aerated at high pressures and then transferred into a tank at atmospheric pressure. The change in pressure creates fine air bubbles that rise and carry the insoluble particles and nonaqueous phases of compounds to the surface. The floating material is then skimmed off the surface. The flotation process can be enhanced by the addition of surfactants.

Density separation is of questionable use in removal of hazardous wastes because of the sludge that results from both sedimentation and flotation processes (Ehrenfeld and Bass, 1984). In addition, complete removal of the hazardous materials may not be achieved. The dissolved air flotation process may also produce hazardous emissions which should be treated appropriately.

Filtration--

Filtration is an effective method that separates low levels of solids from an aqueous phase by passing the waste mixture through a semi-permeable medium (Ehrenfeld and Bass, 1984). In addition to producing a purified filtrate, filtration also decreases the volume or dewaters the waste mixture to produce a sludge concentrate. There are three types of filtration units: granular media filters, rotary drum vacuum filters, and filter presses. Granular media, such as sand, is used to filter suspended solids by gravity or auxiliary pressure. The system is most efficient at filtering aqueous wastes, whereas filtration efficiencies for nonaqueous liquid wastes, slurries, and sludges are moderate to low. The filter bed is regenerated by backwashing and removing solids by flocculation or sedimentation. This type of filtration removes suspended solids down to the 1 to 10 mg/L range.

The rotary drum vacuum filters are constructed by stretching fabric or wire mesh over a drum and small roller (Ehrenfeld and Bass, 1984). The drum is partially submerged in the aqueous mixture which is drawn into the drum by a vacuum. The filtrate is collected and the trapped solids are removed from the filter. The rotary drum vacuum filter can be used for slurries and sludges in addition to aqueous and nonaqueous liquid wastes; sludges can be dewatered by 60 to 90 percent, but high concentrations of suspended solids still remain in the filtrate.

The filter press is constructed with a series of plates and screens which trap solids by squeezing the water out of the waste mixture (Ehrenfeld and Bass, 1984). This type of filtration system is often used to dewater viscous sludges in addition to slurries, and aqueous and nonaqueous liquid wastes. Sludges can be dewatered by 50 to 85 percent, but high concentrations of suspended solids still remain in the filtrate.

In general, the efficiency of filtration can be reduced by clogging the filter bed or fabric medium. In addition, filtration of hazardous wastes results in trapped suspended solids or dewatered sludges that are also hazardous. Dissolved hazardous compounds may not be removed by the filtration process and thus require further treatment.

3. Biological Treatment

Ground water can be withdrawn and treated by conventional biological wastewater treatment processes. Treatment processes used to treat contaminated ground water and leachate from hazardous wastes include: 1) suspended growth processes such as activated sludge, lagoons, waste stabilization ponds and fluidized bed reactors, and 2) fixed film processes such as trickling filters, rotating biological discs, sequencing batch reactors and others. The wastewater can be treated on site by one of these processes or off site at a municipal or commercial treatment plant. A short discussion of each process follows with regards to hazardous waste management. More detailed discussions of these processes are presented in Johnson, 1978; J. R. B. Associates, 1982; Ehrenfeld and Bass, 1984; Shuckrow et al., 1980; Nyer, 1985; and Canter and Knox, 1985.

Biological Wastewater Treatment Processes--

The most commonly used municipal wastewater treatment process, activated sludge, has a number of advantages for treatment of contaminated ground waters. The units include an aeration basin, a clarifier, and sludge recycle. Following treatment in the aeration basin, a portion of the sludge collected in the clarifier is recycled. The recycling process allows an acclimated microbial population to build up in the system, hence the name activated sludge. The settled sludge can adsorb heavy metals and some organics which may cause the sludge to be considered a hazardous waste (Shuckrow et al., 1980). However, some compounds are removed by volatilization during the aeration step (Eckenfelder et al., 1985). Activated sludge treatment can reduce the soluble biochemical oxygen demand (BOD) to less than 10 mg/L and the total BOD, including suspended solids, to less than 30 mg/L. The retention time is short and consequently the process is sensitive to toxic and hydraulic shocks. A survey of 92 industrial wastewater streams conducted by the EPA reported mean BOD removal efficiencies of 86 percent (Ehrenfeld and Bass, 1984). Specific organic compounds can be degraded to low levels; effluent levels of phenol as low as 0.02 mg/L have been reported (Nyer, 1985).

The sequencing batch reactor is an application of the activated sludge process which may be used to treat hazardous waste leachates (Ying et al., 1986). The process involves five steps per cycle: 1) fill-the wastewater is drawn into the vessel where some of the activated sludge from the previous cycle remains, 2) react-aeration and mixing occur, 3) settle-clarification occurs in this step, 4) draw-the supernatant is withdrawn, and 5) idle-the system remains idle until the next cycle is initiated. Treatment of hazardous waste with the sequencing batch reactor may be advantageous because the process is more complete and flexible than other treatment technologies and can provide intermittent treatment; in addition, the same tank can be used for both treatment and clarification. Up to 90 percent of the TOC from a hazardous waste leachate was removed under a 24-hour cycle with a 10-day retention time (Ying et al., 1986).

Like activated sludge, surface impoundments such as aerobic lagoons, facultative lagoons, anaerobic lagoons, and waste stabilization ponds rely on suspended microbial populations to degrade organic material; unlike activated sludge, the biomass is not recycled (Wilkinson et al., 1978; Ehrenfeld and Bass, 1984). Even though the processes typically require less energy and supervision than activated sludge, the operational controls are not as flexible (Shuckrow et al., 1980). The retention time of waste in a surface impoundment is often on the order of weeks whereas that of activated sludge may take a few hours. In general, surface impoundments are quite large, and their size allows for dilution and buffers fluctuations in organic load. Aerobic lagoons are aerated mechanically or by diffusion to increase the degradation rate of organic material and mix the system (Johnson, 1978; Eckenfelder et al., 1985; Ehrenfeld and Bass, 1984). Organic material is degraded aerobically at the surface and anaerobically

19

near the bottom of facultative lagoons (Ehrenfeld and Bass, 1984). Because aeration is not forced or used, facultative and anaerobic lagoons offer the advantage of easy operation and low cost (Shuckrow et al., 1980); however, anaerobic processes result in incomplete degradation of organic compounds and hence low quality effluent. Facultative lagoons can also tolerate higher organic loading than aerobic lagoons and both facultative and anaerobic lagoons may generate noxious odors (Eckenfelder et al., 1985). Anaerobic processes are enhanced in anaerobic lagoons by low surface to volume ratios (Ehrenfeld and Bass, 1984). Waste stabilization ponds are lagoons that are aerated by natural processes such as wind and photosynthesis (Ehrenfeld and Bass, 1984). The ponds are principally a polishing technique for low organic waste waters (Johnson, 1978). The ponds are usually 0.3 to 0.6 m in depth (Ehrenfeld and Bass, 1984). Removal efficiencies for surface impoundments are in the range of 60 to 90 percent. They are sensitive to shock loadings of toxic chemicals and fluctuations in temperature.

Fluidized bed reactors are filled with materials such as sand or coal that are suspended by wastewater which flows upward through the material (Wilkinson et al., 1978). The particles are colonized by a dense growth of microorganisms which rapidly degrade organic material present in the waste stream.

In the fixed film process, wastewater is passed over a surface colonized with microorganisms; the attached biofilm degrades the organic material. The original fixed film process, the trickling filter, uses a solid medium such as rock or plastic, as the surface for microbial attachment (Canter and Knox, 1985). Trickling filters can remove from 60 to 85 percent of the BOD (Eckenfelder et al., 1985). Suspended or colloidal organics can be treated, and the process is usually limited to low organic loadings (J. R. B. Associates, 1982).

Trickling filters that are operated anaerobically are known as anaerobic filters (Eckenfelder et al., 1985). The anaerobic filter process can tolerate high loading rates. Low pH and inorganics such as sodium, sulfate, and heavy metals may inhibit methanogenesis and toxic organics may also be a problem (Rittman and Kobayshi, 1982). The biological tower is another variation of the trickling filter. The tower is packed with a colonizable surface which may reach a height of 16 to 20 feet (Canter and Knox, 1985). The process operates in a countercurrent mode; contaminated water is sprayed on the top of the tower as air is pulled from the bottom.

A rotating biological disc is similar in concept to trickling filters. Discs or drums which are coated with a biofilm are partially submerged and rotated through the wastewater (Wilkinson et al., 1978; Ehrenfeld and Bass, 1984). Rotation of the discs aerates the attached biofilm. The process is sensitive to shock loading and temperature fluctuations, but is otherwise moderately reliable (J. R. B. Associates, 1982). In comparison to activated sludge, rotating biological discs require less energy and are easier to operate, but are similar in effectiveness (Eckenfelder et al., 1985). Clarification may be required before and after treatment of wastewater with rotating biological discs (Ehrenfeld and Bass, 1984).

Biological wastewater treatment processes may be used to treat the following classes of organic compounds typically found in ground water: alcohols, organic acids, aldehydes, ketones, quinones, amines, amides, carbohydrates, esters, some ethers, phenolics, and some aromatics (Absalon and Hockenbury, 1983; Eckenfelder et al., 1985). Compounds that may be difficult to treat with biological wastewater processes include halocarbons, high molecular weight polynuclear aromatics, pesticides, and organometals (Ehrenfeld and Bass, 1984).

Examples of Withdrawal and Biological Treatment--

Biological wastewater treatment processes have been used in remedial action at several hazardous and nonhazardous waste sites. Adequate treatment of leachates from recent municipal refuse landfills that contained high levels of free fatty acids was achieved by biological treatment (Chian, 1977). Leachates from older landfills may be more amenable to physical-chemical treatment processes. In a pilot study, Stover and Kincannon (1982) were able to decontaminate ground water from a hazardous waste site using activated sludge. The batch activated sludge pilot system was seeded with organisms that were acclimated to the same compounds found in the contaminated ground water - phenols, cresols, dichlorobenzenes, and others. Following acclimation and stabilization of the batch activated sludge for three weeks, the organisms were able to reduce the total phenols, TOC, BOD, and chemical oxygen demand by 80 percent or more within 24 hours.

Combinations of Biological Treatment With Other Processes--

Combinations of conventional biological wastewater treatment with other water treatment processess such as granular activated carbon (GAC), air stripping, and addition of acclimated bacteria have also been successful. Feasibility studies on decontamination of leachate from the Ott/Story hazardous waste site in Muskegon, Michigan have combined activated sludge and GAC adsorption to remove various halogenated aliphatics, benzene, and toluene (Shuckrow and Pajak, 1981). Initial attempts to acclimate an activated sludge culture to the organic contaminants were minimally successful and the addition of a commercial microbial culture was not effective; however, a combination of GAC adsorption followed by activated sludge removed greater than 95 percent of the TOC. The activated sludge organisms removed the organics that were not sorbed in the GAC treatment. Treatment efficiencies were greater than 75 percent as long as the removal efficiency of the GAC was high. Anaerobic treatment combined with GAC was less effective than aerobic treatment (activated sludge) and suffered the same decline as the aerobic process when the GAC was saturated (Shuckrow et al., 1980). Removal of TOC by a treatment train using GAC followed by anaerobic and then aerobic biological treatments was also tested (James et al., 1981). The biological treatment steps were not necessary when the GAC sorption sites were not significantly saturated; however, the biological treatment increased the removal efficiency of the treatment train as more GAC sorption sites became saturated. The TOC removal efficiency of GAC combined with anaerobic and aerobic treatment was less than that of GAC and aerobic treatment only.

Josephson (1983) reported that a combination of powdered activated carbon and activated sludge was used to treat ground water contaminated with hydrocarbons, pesticides, and other organics. A removal efficiency of 95-99 percent was achieved for the COD, total nitrogen, and various organics.

Air stripping followed by biological treatment was used in a pilot study to treat ground water contaminated with trichloroethylene, freon, 1,2-dichloroethene, toluene, ethyl benzene, xylenes, vinyl chloride, acetone, isopropanol, o-dichlorobenzene, 1,1-dichloroethylene, and 1,2-dichlorophenol (Schaezler and St. Clair, 1985). Air stripping could remove all of the organics except for the nonvolatile compounds isopropanol and acetone; however, a treatability study indicated that the nonvolatile compounds were biodegradable. Hence, a treatment system utilizing both air stripping and biological treatment was recommended for this site.

Nyer and Sauer (1984) described the cleanup of shallow ground water from a Gulf Coast hazardous waste site. The saline aquifer was contaminated with 400 mg/L phenol and other organics which resulted in a TOC concentration of 1,300 mg/L. Several options that were considered for treatment are reported with estimated costs per gallon in parenthesis: pond evaporation with oxygen and nutrient addition ($0.028); deep well injection ($0.183); solidification/adsorption to concentrate the liquid and then adsorb the material to trench backfill ($0.085); granular activated carbon adsorption ($0.058); biological treatment ($0.005).

A feasibility study indicated that the organics were biodegradable, but carbon adsorption would be required as a polishing technique (Nyer and Sauer, 1984). The overall treatment system would consist of: 1) pH adjustment, 2) chemical addition, 3) biological treatment with two aeration basins, a clarifier, and a fixed activated sludge treatment system (FAST), 4) filtration through a dual media filter, and 5) carbon adsorption. The FAST system uses particles of plastic colonized by bacteria in a well mixed tank. The system is essentially a hybrid of activated sludge and fixed film processes. The biological system was seeded with activated sludge from a refinery that treated ballast from oil tankers. Results from the pilot plant, which included the aeration plant and clarifier only, indicated that the TOC was reduced by 70 percent. Addition of the FAST system, the dual media filter, and the carbon adsorption unit to the treatment train reduced the concentration of TOC from 1,300 to 18 mg/L (98 percent) (Nyer, 1985).

Addition of mutant bacteria to a sequencing batch reactor, a process patented in 1985 by Colaruotolo et al. (1985b), was used to treat leachate collected from the Hyde Park Landfill in Niagara Falls, New York (Ying et al., 1986). The leachate contained chlorinated organics, phenol, and benzoic acid. A consortium of microorganisms that could degrade most of the contaminants was isolated from the leachate; however, degradation of the pollutants by bacterial strains in the consortium was variable (Sojka et al., 1986). By genetic manipulation, organisms in the consortium that could degrade the remaining compounds were found. Tests with bench scale

sequencing batch reactors and also pilot-plant scale units indicated that the TOC was reduced by 85 percent or greater and that individual contaminants were generally reduced by 95 percent or greater. The biomass yield was 0.64 mg/mg feed TOC. Amendments of nitrogen and phosphorous did not improve treatment over the addition of only nitrogen. Cost savings for the biological treatment over the existing carbon adsorption system were estimated to range from $538,000 up to $783,000.

Bartha (1986) suggested that inoculation of microorganisms into a wastewater treatment process be judged with caution. Inoculation may be useful for startup, disruptions, for certain xenobiotics that cannot be degraded by the natural flora, or when the added organisms cannot sustain themselves.

D. In Situ Physical and Chemical Treatment

In situ treatment techniques are similar to methods used to treat waste after withdrawal or excavation and methods used to solidify or stabilize a waste for safer transportation and disposal (Ehrenfeld and Bass, 1984). In situ remedial action is a direct application of these techniques to the waste in place. Treatment in place avoids the cost of withdrawal or excavation and disposal after the treatment; the concept is also desirable because there is little or no visible disturbance of the environment. Also, large quantities of soil can be treated at once (Truett et al., 1982). In addition, in situ treatment may be more effective than withdrawal and treatment; under certain hydrogeological conditions, incomplete recovery of the pollutants occurs using conventional pumping techniques (Ehrenfeld and Bass, 1984). However, in situ techniques may have to be used with physical containment measures to prevent further migration of the pollutants (Truett et al., 1982).

In situ treatment must be preceded by a thorough hydrogeological investigation of the site and characterization of the waste (Ehrenfeld and Bass, 1984). Physical and chemical treatments are usually applied to homogeneous wastes for optimum results and the treatment is waste-specific. The major limitation of in situ physical/chemical remediation is the potential to create additional pollution or volatilize toxic chemicals during the process (Ehrenfeld and Bass, 1984).

Chemical treatment involves neutralizing, precipitating, oxidizing or reducing, or destroying the contaminants by injecting the reactive material into the waste (Ehrenfeld and Bass, 1984). The chemical is added into injection wells to treat plumes of leachate and ground water, therefore, the extent of the plume must be well defined for thorough treatment. The reactive agent is added directly to the waste contained in surface impoundments or landfills.

In situ chemical treatment requires that the waste be homogeneous and that the characteristics and concentrations of the contaminants are known. Examples of chemical treatment are the oxidation of cyanide with strong oxidizing agents such as sodium hypochlorite, precipitation of metals with alkali agents or sulfides, and the precipitation of hexavalent chromium using reducing agents (Ehrenfeld and Bass, 1984). The addition of activated carbon directly to a surface impoundment or landfill is an example of in situ physical treatment.

A plume of leachate or contaminated ground water can be directly treated using permeable treatment beds or by chemical injection (Ehrenfeld and Bass, 1984). Permeable treatment beds are constructed by excavating trenches downgradient of the plume. The trenches are excavated through the aquifer and into the consolidated zone. The trench is then capped to prevent percolation of rain or runoff into the treatment area. The width of the trench depends on the permeability of the chosen fill material, the velocity of ground water flow, and the time required to react the contaminants with the fill material. The technique is amenable to shallow aquifers only because of the construction design. The trenches are then filled with permeable materials which neutralize or precipitate the contaminants. Materials such as limestone or crushed shell, activated carbon, glauconitic green sand (actually a clay with high metal adsorbing capacity), zeolites, and synthetic ion exchange resins are used to fill the trench. Most of these materials are somewhat effective in removing heavy metals. Limestone can be used to neutralize acidic plumes while lipophilic organic compounds can be removed by activated carbon. The effectiveness of permeable treatment beds is short-lived because the fill material becomes plugged. The plume may escape treatment because the ground water is diverted around the trench or is channeled through the fill material. In addition, changes in the composition of the plume may affect the contact time and reduce removal efficiencies.

22

In situ chemical treatment of a formaldehyde spill was conducted using an alkaline solution of hydrogen peroxide (Sikes et al., 1984). About 15,000 square ft of formaldehyde-contaminated soil was first treated with a buffered solution of sodium hydroxide and soda ash (pH 9.5) and then amended in two separate treatments with a 5 percent solution of hydrogen peroxide. The oxidation rate of formaldehyde by hydrogen peroxide had been observed to proceed faster at alkaline pH in laboratory tests. The formaldehyde concentration was reduced from 30,000 ppm to a range of 500 to 1000 ppm after both treatments. The in situ chemical treatment with hydrogen peroxide was then followed by biological treatment.

Removal of iron and manganese from ground water by the Vyredox method is an example of an in situ chemical treatment (Hallberg and Martinell, 1976; Zienkiewicz, 1985). The process is used to remove these metals before the ground water is used for industrial purposes or drinking water. The iron and manganese are precipitated out of solution in an oxidized state by perfusing the aquifer with oxygen-rich water. Iron and manganese oxidizing bacteria may be involved in the oxidation reactions; however, microbial participation is not well defined. The oxidizing conditions maintain high Eh and pH values and the metals precipitate in the strata before reaching the production well.

Contaminants may be stabilized in the subsurface by polymerization reactions. Williams (1982) reported that an underground spill of an acrylate monomer was polymerized in place by injecting a catalyst and activator into the area of contamination. The acrylate monomer is a moderately water soluble liquid that is less dense than water. Two treatments with a catalyst and an activator four days apart polymerized 85-90 percent of the liquid monomer into a solid.

Solution mining, or extraction, is another type of in situ physical treatment process (Ehrenfeld and Bass, 1984). Chemical processing and mining industries have been using chemical extraction techniques for years. In situ treatment of hazardous waste involves application of a solvent to the waste in place and then withdrawal of the elutriate using a well point system. The type of compounds removed by this process depends on the characteristics of solvent used and the contaminants present. Solvents used in the process include water, acids, ammonia, and/or chelating agents. Laboratory tests should be conducted to determine the extraction efficiency of the solvent for the target contaminants. Problems that may be encountered include the incompatibility of the solvent with some compounds in the waste. Also, injection of the solvent into the subsurface may create additional contamination. The elutriate is also considered hazardous and will require treatment or proper disposal. The process is largely undemonstrated for in situ remediation; however, metal extraction from some hazardous materials has been successful in laboratory studies. Ellis et al. (1984) conducted both column and batch experiments and found 90 percent or greater extraction efficiencies for aromatic and intermediate molecular weight aliphatic hydrocarbons, polychlorinated biphenyl mixtures, and chlorinated phenol mixtures from soil by water washing and surfactant solutions.

In situ vitrification is a physical treatment process in which waste and soil are heated to melting and then cooled to form a glassy, solid material that resembles obsidian (Ehrenfeld and Bass, 1984; Battelle Labs, 1985). Battelle-Northwest has developed a vitrification process which uses electric-joule heating. An electric current is passed through the waste from electrodes that are placed around the site; the waste is melted from the top down. The process is amenable to inorganic and nonvolatile organic compounds/soil mixtures. Treatment of some volatile organics may release toxic fumes; however, Battelle-Northwest has devised a covering hood to trap any escaping gases from the treatment area. The trapped gases are then treated in an off-gas processing system.

The resulting vitrified material is about twice as strong as unreinforced concrete with permeabilities that approximate those of Pyrex glass (Battelle Labs, 1985). In addition, the glass-like material should not pose any environmental risks for thousands of years. The disadvantages of the process are related to energy consumption. About 2000 kw/m^3 and a melting temperature of 1700°C are required to vitrify the waste.

Another type of in situ soil decontamination process similar to vitrification is radio frequency (RF) in situ heating (Dev et al., 1984). The process was originally developed to heat large amounts of earth, such as oil shale or tar sand, to recover hydrocarbons. The waste site is heated with electromagnetic waves with frequencies between 2 and 45 MHz. A series of horizontal conductors are placed above the surface of the site and excited with a radio

23

frequency generator. The organic pollutants are decontaminated by thermal decomposition, vaporization, and distillation when heated for one to two weeks at temperatures between 300 to 400°C. The resulting gases that move to the surface are collected by a vapor barrier and disposed of appropriately. The disadvantage of the RF heating process is the large energy requirement. In addition, a large amount of the applied heat may be lost because of thermal conduction. However, treatment of a hazardous waste landfill by RF in situ heating is thought to be two to four times cheaper than incineration. The RF method is also advantageous because treatment is in place, the waste is safely contained, small amounts of additional wastes are generated, and exposure to operating personnel is minimal.

Another type of innovative physical process for in situ decontamination is the application of a vacuum in the vadose (unsaturated) zone. The process can be used to monitor or recover subsurface contaminants from leaking storage facilities, waste sites, or pipelines (Malot, 1985). Monitoring the unsaturated zone can provide information concerning the potential for contamination of the ground water. Volatile organic compounds, solvents, and petroleum-derived compounds are most amenable to treatment by this technique. Volatile tracers can be added to tanks that contain nonvolatile compounds to verify potential leaks. The system is composed of a subsurface extraction well and a vacuum source; recovery operations also include surface equipment for collection or treatment and a probe submerged in the extraction well to monitor effectiveness. Each system design is site specific and must be installed to accommodate the field constraints. The effectiveness of the technique has been demonstrated (Agrelot et al., 1985). Vacuum extraction of organic contaminants is low cost because of the high removal efficiencies in comparison to other techniques; the process can simultaneously remove free product, residual hydrocarbons and vapors (Malot and Wood, 1985). In addition, decontaminating the vadose zone is important because the source for pollutant entry or recharge into the aquifer is eliminated. Vacuum extraction can also be used to recover floating product from perched water tables when recovery is difficult using a pumping well; movement of floating product to an extraction well is difficult to induce when the perched water is thin.

The vacuum concept has also been used to solely vent vapors that result from hydrocarbon spills in the subsurface (Crow and Minugh, 1985). The process was tested in a pilot-scale field study in which two test systems were installed at a spill site where the hydrocarbon resided on shallow ground water; pure product was recovered using conventional techniques. Each unit was composed of vapor monitoring probes, a vapor extraction well that operated by negative pressure, and air inlet wells for entry of atmospheric air into the subsurface; two liquid ring pumps supplied the vacuum source for venting. The results from the study indicated that the technique was effective in controlling and eliminating vapors from the vadose zone; however, pulse venting may be more cost effective because removal of the vapors required less time than reestablishing baseline vapor concentrations in the vadose zone. The major limitation of the process is that vapors that are removed must be treated or released into the atmosphere. The technique is largely undemonstrated and future studies are planned for further modification.

Coia et al. (1985) used positive pressure, or air stripping, to remove volatile chlorinated organics from contaminated soils in a pilot field study. The volatile compounds were extracted from the vadose zone as a vapor by forced ventilation. The design included a pipe vent, air ventillation system, and controls to monitor the removal process. The stripping was accomplished by continuous injection and extraction of air through the pipe vents; the extracted air is then passed through activated carbon before release to the atmosphere. The system was effective in removing the chlorinated compounds from the vadose zone; however, further research is needed to determine the effect of soil type and the presence of perched water on the process.

E. In Situ Biological Treatment

1. Microbial Activity In Aquifers

Microbial processes may be used to degrade contaminants in situ by stimulating the native microbial population. Another in situ biostimulation technique which is not yet demonstrated is the inoculation of the subsurface with a microbial population that has specialized metabolic capabilities. Even in the presence of an indigeneous population which is acclimated to the organic contaminants, degradation may be limited at high contaminant concentrations or by some environmental factor. Addition of electron acceptors, such as oxygen, and inorganic nutrients, typically nitrogen, phosphorus, and trace metals, may provide the microflora with essential nutrients that

are limiting in the presence of high concentrations of pollutants. Inoculation of a specialized microbial population may reduce the time required for acclimation to the contaminants and/or allow the removal of recalcitrant contaminants. Related processes such as the addition of bioemulsifiers or surfactants to increase the availability of subsurface contaminants to the microflora can also be used. When applicable, biological processes may offer the advantage of partial or complete destruction of the contaminants rather than simply transferring the pollution to another phase of the environment.

Technologies for biorestoration of polluted aquifers have resulted from recent research indicating that subsurface microorganisms exist, are metabolically active and often nutritionally diverse. A review, published by Dunlap and McNabb (1973) of the Robert S. Kerr Environmental Research Laboratory, addressed subsurface biological activity in relation to ground water pollution and initiated most of the research in this area . Before publication of the review, the concept of biological activity below the rhizosphere had not been widely received. Microbiologists were skeptical about biological activity in the subsurface because of oligotrophic conditions below the rhizosphere (Leenheer et al., 1974) and an early study which had indicated that microbial numbers decreased precipitously with depth (Waksman, 1916).

Sampling Methods for Subsurface Microbes--

A document that described sampling methods for subsurface microorganisms was published in 1977, by the Environmental Protection Agency (Dunlap et al., 1977). The method for procuring a representative sample of unconsolidated subsurface soil has since been modified (Wilson et al., 1983). A soil sample is collected by first drilling a borehole to a desired depth with an auger and then taking the sample with a core barrel. After sample procurement, the core is extruded through a sterile paring device that removes the outer layer of soil that has come in contact with the core barrel. The remaining soil core is thus uncontaminated by the sampling procedure and representative of the subsurface.

Investigations of microbial activity in the subsurface conducted prior to the development of the sampling techniques were equivocal because of the potential for contamination during sample procurement. In addition, many of the investigations were conducted using well water instead of core material. Recent evidence suggests that the majority of subsurface microorganisms are associated with soil particles (Harvey et al., 1984). In addition, well water may contain microorganisms that are artifacts of the well because of subsurface contamination during well installation and changes in water quality around the well.

Microbial Numbers in the Subsurface--

Methods to enumerate the subsurface microflora also have been developed. Electron microscopy, viable counts, epifluorescence microscopy, and measurements of biochemical components have been used to estimate microbial biomass (Ghiorse and Balkwill, 1985; Ghiorse and Balkwill, 1983; Wilson et al., 1983; Smith et al., 1986; Stetzenbach et al., 1986; Smith et al., 1985; Balkwill and Ghiorse, 1985; Bone and Balkwill, 1986; Webster et al., 1985; White et al., 1983; Hoos and Schweisfurth, 1982; Ehrlich et al., 1983; Federle et al., 1986). In contrast to Waksman's study (1916) which reported that microbial numbers declined with depth, uniform population levels around 10^6-10^7 cells/g dry soil, measured by epifluorescence microscopy, were reported for profiles of uncontaminated shallow aquifers (Ghiorse and Balkwill, 1985; Webster et al., 1985; Wilson et al., 1983; Ghiorse and Balkwill, 1983; Balkwill and Ghiorse, 1985; Bone and Balkwill, 1986). However, bacteria in a chalk aquifer (consolidated) were sporadically distributed with depth (Towler et al., 1985). Close examination of the subsurface strata indicates patchiness of bacterial populations; samples from the top of the unsaturated zone of an artesian aquifer yielded the highest counts whereas those from bedrock and confining layers yielded the lowest total counts (Beloin et al., 1986).

Microbial Ecology of the Subsurface--

Bacteria are the predominant form of microorganism observed in the subsurface although a few higher life forms have been detected (Wilson et al., 1983; Ghiorse and Balkwill, 1985; White et al., 1983). Some eucaryotic forms

which may be fungal spores or yeast cells have been observed in the upper 10 m of a soil profile (Ghiorse and Balkwill, 1983; Hoos and Schweisfurth, 1982; Federle et al., 1986). Bacteria, protozoa, and fungi have been detected in samples of ground water collected from one-year-old wells (Hirsch and Rades-Rohkohl, 1983). In addition, a slow-growing amoeba has been isolated and cultured from the ground water interface of an uncontaminated soil (Balkwill and Ghiorse, 1985; Beloin et al., 1986).

Metabolic Activity of the Subsurface Microbial Community--

Organic matter that enters the uncontaminated subsurface is usually the more refractory humic substances which resist degradation while percolating through the biologically active soil zone. The organic material available for metabolism by the subsurface microflora is likely to be in low concentration and difficult to degrade. The majority of microorganisms present in such nutrient-poor environments are generally oligotrophic. Characterization of the subsurface microflora indicates that the bacteria are usually smaller (<1.0 mm in size) than those in eutrophic environments and both Gram positive and negative cell types are present (Ghiorse and Balkwill, 1983; Wilson et al., 1983; Ghiorse and Balkwill 1985). Gram positive forms predominate in many uncontaminated soils. The predominance of small, coccoid cells and hence a large surface to volume ratio for enhanced nutrient uptake, is a likely mechanism for survival in an oligotrophic environment such as the uncontaminated subsurface (Wilson et al., 1983). In contrast, subsurface soil contaminated with creosote waste was found to contain more biomass and a greater proportion of Gram negative to Gram positive microbes when compared to uncontaminated soil from the same site (Smith et al., 1985; Smith et al., 1986).

Studies have also indicated that many subsurface microorganisms are metabolically active. Of the total cell count, about 0.01 to 50 percent can be recovered by plating on solid media and about 1 to 10 percent exhibit respiratory activity measured by the reduction of 2-(p-iodophenyl)-3-p-nitrophenyl)-5-phenyl tetrazolium chloride by cytochromes (Balkwill and Ghiorse, 1985; Webster et al., 1985). Microbial activity, measured by the hydrolysis of fluorescein diacetate, declined with depth in the unsaturated zone of Ultisols and Alfisols (Federle et al., 1986); however, 2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyl tetrazolium chloride reduction varied greatly between strata of a soil profile obtained from a shallow aquifer (Beloin et al., 1986).

Many subsurface microorganisms are nutritionally diverse (Table 2-3). Simple substrates such as glucose, glutamic acid, arginine, a mixture of amino acids, and a synthetic compound, nitrilotriacetic acid, were mineralized in samples of uncontaminated ground water (Larson and Ventullo, 1983). Polar solvents such as acetone, isopropanol, methanol, ethanol, and tert-butanol also have been reported to degrade aerobically by subsurface microorganisms (Novak et al., 1984; Jhaveri and Mazzacca, 1983). More challenging contaminants that are aerobically degraded by subsurface microorganisms include the methylated benzenes, chlorinated benzenes (Kuhn et al., 1985), chlorinated phenols (Suflita and Miller, 1985), and methylene chloride (Jhaveri and Mazzacca, 1983). Highly lipophilic compounds such as naphthalene, methylnaphthalenes, dibenzofuran, fluorene, and phenanthrene are also biotransformed in the subsurface (Wilson et al., 1985; Lee and Ward, 1985).

The microflora in some uncontaminated soils require little or no acclimation period to degrade many xenobiotics. For example, toluene, chlorobenzene, and bromodichloromethane were biotransformed in uncontaminated soil, but not 1,2 dichloroethane, 1,1,2-trichloroethane, trichloroethylene, and tetrachloroethylene (Wilson et al., 1983). Benzene, toluene and the xylene isomers were found to degrade in uncontaminated subsurface soils (Barker and Patrick, 1986). In addition, methanol (80-100 ppm) was degraded completely after two months, whereas tert-butanol degraded much slower in two uncontaminated anaerobic aquifers (White et al., 1986).

In contrast to reports of degradation of xenobiotics in uncontaminated soil, long periods of acclimation to subsurface pollutants may be required before biodegradation can occur. Wilson et al. (1985) reported degradation of naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, dibenzofuran and fluorene at 100-1000 mg/l in subsurface soil in the plume of contamination from a creosote waste pit; however, degradation of these compounds was not observed in uncontaminated soil from the same site. The time and concentration required for acclimation of the microflora to subsurface pollutants are unknown. Spain and Van Veld (1983) reported a threshold concentration of 10 ppb for adaptation to p-nitrophenol in samples of sediment and natural water. A better understanding of acclimation processes may explain why some chemicals persist in the subsurface even though they have been reported to degrade in laboratory cultures and samples of water and soil.

26

Table 2-3. Organic Compounds That Have Been Shown to be Biodegradable in the Subsurface

Compound	Soil from Contaminated Area	Aerobic	Reference
Natural Compounds			
glucose	no	yes	Larson and Ventullo, 1983
glutamic acid			
arginine			
Solvents			
acetone	yes	yes	Jhaveri and Mazzacca, 1983
ethanol			
isopropanol			
tert-butanol	yes	yes	Novak et al., 1984
methanol			
bromodichloromethane	no	yes	Wilson et al., 1983
Aromatics			
benzene	no	yes	Barker and Patrick, 1983
xylene			
methylated benzenes	yes	yes	Kuhn et al., 1985
chlorinated benzenes			
chlorinated phenols	yes	yes	Suflita and Miller, 1985
naphthalene	yes	yes	Wilson et al., 1985; Lee and Ward, 1985
dibenzofuran			
fluorene			
phenanthrene			
toluene	no	yes	Wilson et al., 1983
chlorobenzene			

Environmental Factors Which May Limit Biodegradation--

Environmental factors may limit or preclude the biodegradation of subsurface organic pollutants, even in the presence of adapted organisms. Recalcitrance of compounds thought to be biodegradable may result from lack of an essential nutrient, substrate concentration, substrate inaccesibility,and the presence of toxicants (Alexander, 1975). Transport of contaminants in the subsurface also affects biodegradation. Transport is discussed in detail in Section II.F.

Biodegradation of many organic pollutants in the subsurface may be limited by insufficient oxygen. Alexander (1980) reported that even the metabolism of carbohydrates may be inhibited in oxygen-depleted environments. Lee and Ward (1985) found that the rate and extent of biotransformation of naphthalene, 2-methyl naphthalene, dibenzofuran, fluorene, and phenanthrene were greater in oxygenated ground water than in oxygen-depleted water. Contrary to general theory that complete degradation (mineralization) of hydrocarbons requires molecular oxygen, more recent research suggests that alternate pathways exist under anaerobic conditions. Kuhn et al. (1985) reported mineralization of xylenes in samples of river alluvium under denitrifying conditions. In addition, benzene, toluene, the xylenes, and other alkylbenzenes were metabolized in methanogenic river alluvium that had been contaminated with landfill leachate (Wilson and Rees, 1985); mineralization of toluene was confirmed by adding ^{14}C-labelled toluene and measuring the amount of $^{14}CO_2$ produced. Grbic-Galic and Vogel (1986) also reported mineralization of toluene and benzene under anaerobic conditions by a methanogenic consortium acclimated to ferulate. Further tests indicated that water supplied the oxygen that is first incorporated into the toluene and benzene ring (Vogel and Grbic-Galic, 1986).

The presence of oxygen may inhibit the biodegradation of many halogenated aliphatic compounds in the subsurface. Degradation of trihalomethanes, trichloroethylene, and tetrachloroethylene did not occur in aerobic cultures of sewage bacteria; however, the trihalomethanes were degraded anaerobically by mixed cultures of methanogens (Bouwer et al., 1981). In addition, Bouwer and McCarty (1983b) reported that chloroform, carbon tetrachloride and brominated trihalomethanes, but not chlorinated benzenes, ethylbenzene, or naphthalene were biotransformed under denitrifying conditions.

In addition to oxygen, other nutrients may limit the biodegradation of organic pollutants in the subsurface. Inorganic nutrients, such as nitrogen and phosphorous, may be limiting when the ratios of carbon to nitrogen or phosphorous exceed that necessary for microbial processes. On the other hand, the presence of sulfate may inhibit methanogenic consortia that have been reported to dehalogenate and mineralize many chlorinated aromatic compounds (Suflita and Gibson, 1985; Suflita and Miller, 1985).

The effect of substrate concentration on biodegradation of organic compounds in surface soils and waters has been documented (Alexander, 1985). Thresholds below which degradation is slow or does not occur may exist for compounds that are readily biodegradable at higher concentrations. Boethling and Alexander (1979) reported that less than 10 percent of 2,4-dichlorophenoxyacetate at concentrations of 22 pg/ml and 2.2 ng/ml was mineralized in stream water whereas about 80 percent was mineralized at higher concentrations of 0.22 and 22 mg/ml. On the other hand, microorganisms may be inhibited or killed by high concentrations of organic pollutants that result from injection wells and hazardous waste sites. Lee (1986) reported that glucose mineralization was inhibited in subsurface soil heavily contaminated with creosote; however, glucose was mineralized in uncontaminated and slightly contaminated core material from the same site.

Other factors such as sorption, pH and temperature may also affect biodegradation of pollutants in the subsurface. Many of the organic compounds contaminating the subsurface are highly lipophilic. These compounds are sorbed by soil more strongly than the more hydrophilic compounds (Hutchins et al., 1985). Sorption may enhance degradation by concentrating nutrients or conversely, prevent degradation by rendering the substrate unavailable to the microorganism. Zobell (1943) reported that sorption of organic material to solid surfaces in dilute nutrient solutions increased microbial respiration. In contrast, Ogram et al. (1985) observed that 2-4 dichlorophenoxy acetic acid sorbed to soil was completely protected from microbial degradation. Therefore, sorption may be important in nutrient scavenging in uncontaminated aquifers which are generally oligotrophic; however, sorption may compete with the microflora for subsurface pollutants that are relatively hydrophobic.

The soil pH may affect sorption of ionizable compounds in addition to limiting the types of microorganisms in the subsurface. Methanogens, which have been implicated in mineralization of some aromatic hydrocarbons, are inhibited at pH values less than 6.0 (Alexander, 1977). Nitrification, the microbial conversion of ammonia to nitrate, is also limited at pH values below 6.0 and is negligible below 5.0. Hambrick et al. (1980) also reported that mineralization of octadecane and naphthalene in sediment was faster at a pH of 8.0 than 5.0.

28

Temperature also influences microbial metabolism of subsurface pollutants. The temperature of the upper 10 m of the subsurface may vary seasonably; however, that between 9-18 m approximates the mean air temperature (between 3 and 25°C in the United States) of a particular region (McNabb and Dunlap, 1975). Biodegradation of subsurface pollutants in the more northern climates may therefore be limited by cooler temperatures. Bartholomew and Pfaender (1983) reported that the microbial metabolism of m-cresol, nitrilotriacetic acid, and chlorinated benzenes in fresh water and estuarine areas decreased as temperature decreased. Atlas (1975) and Mulkins-Phillips and Stewart (1974b) also reported a direct relationship between petroleum hydrocarbon degradation and temperature.

In summary, the subsurface environment contains microbes that degrade many of the organic compounds that contaminate ground water. The subsurface microorganisms in uncontaminated aquifers are likely to be oligotrophic. The majority of the microorganisms are associated with soil particles. Even in the presence of adapted populations, environmental factors such as temperature, pH, dissolved oxygen levels, inorganic nutrient concentrations, and the availability and concentration of the organic contaminants may limit biodegradation of subsurface pollutants.

2. Biostimulation by Addition of Limiting Nutrients

Development of the In Situ Biostimulation Process with Oxygen Supplied by Air Sparging

Application of the degradative activity of subsurface microbes--The potential for biodegradation of organic compounds in contaminated aquifers was first reported in 1971. Bacteria capable of degrading hydrocarbons were observed in an area contaminated with gasoline; however, biodegradation of the gasoline was limited by the availability of oxygen, mineral nutrients, and hydrocarbon surface area (Williams and Wilder, 1971). Williams and Wilder (1971) suggested that these hydrocarbon-degrading bacteria could be used to clean the aquifer of residual gasoline; however, concern was expressed that bacterial growth would plug the well and formation. Davis et al. (1972) recommended supplying the indigenous microflora with nutrients, oxygen, and moisture rather than inoculating the subsurface with commerical biological products such as dried bacterial cultures. Oxygen-limited degradation of hydrocarbons was reported by McKee et al. (1972) in studies designed to investigate the fate of gasoline trapped in the pore space of sand columns. Several species of Pseudomonas and Arthrobacter were isolated from ground waters associated with a gasoline spill and used in the column experiments. The total number of gasoline-degrading bacteria in the ground water numbered over 50,000 cells/ml in the contaminated zone, but less than 200 cells/ml had been found in the uncontaminated wells and in wells where gasoline had not been detected for a year. The presence of high numbers of gasoline-degrading bacteria was suggested as an indicator of cleanup progress. In the column study, the bacteria rapidly degraded the gasoline in the zone of aeration but slowly degraded that in the saturated zone. In a similar study, Litchfield and Clark (1973) enumerated hydrocarbon-degrading bacteria in ground waters from 12 sites which were contaminated with petroleum. The numbers of hydrocarbon-degrading bacteria ranged from 10^3 to 10^6 cells/ml, with similar numbers of both aerobic and microaerophilic organisms, in ground waters containing more than 10 ppm hydrocarbon. Hydrocarbon-degrading bacteria were found in ground water from all 12 sites; however, on a site by site basis, there were no relationships between the types of organisms, the type of petroleum contamination, the geological characteristics, or the geographical location of the site.

Application of the degradative capacity of subsurface microorganisms to restore gasoline-contaminated ground water was first demonstrated by Raymond, Jamison, Hudson and coworkers at Suntech (Lee and Ward, 1985). In 1974, Raymond (1974) received a patent on a process designed to remove hydrocarbon contaminants from ground waters by stimulating the indigenous microbial population with nutrients and oxygen. Oxygen and nutrients are introduced into the formation through injection wells and production wells were used to circulate them through the aquifer. Placement of the wells was dependent on the area of contamination and the porosity of the formation, but usually no closer than 100 ft apart. The nutrient amendment consists of nitrogen, phosphorus, and other inorganic salts, as required, at concentrations of 0.005 to 0.02 percent by weight; oxygen was supplied by sparging air into the ground water. The process was projected to require about six months to achieve degradation of 90 percent of the hydrocarbons if the growth rate of the microorganisms was 0.02 g/L per day. The numbers of

bacterial cells were expected to return to ambient levels once the addition of nutrients was terminated. The process was expected to be more efficient in treating ground water contaminated with less than 40 ppm of gasoline.

First application of the biostimulation process--A pipe line leak in Ambler, Pennsylvania was the first site where Raymond's patent on biorestoration was demonstrated. An estimated 380,000 L of high octane gasoline had leaked into a highly fractured dolomite outcrop underlaid by quartzite (Raymond et al., 1975). Depth to the water table ranged from 9.2 to 30.5 m in the 46 monitoring wells installed at the site. Before biorestoration was attempted, conventional pump and treat technologies were used as remedial action. Containment of the gasoline was achieved by continuously pumping water from wells located in the spill area. About 238,000 L of the gasoline was recovered by physical methods; however, the recovery program was incomplete and approximately 119,000 L of residual gasoline remained. The concentration of dissolved gasoline in the withdrawn ground water averaged less than 5 ppm. The time required for restoration of the aquifer using this pump and treat technique was estimated to be more than 100 years.

Problems in analyzing the concentration of residual hydrocarbons during the pump and treat phase were later attributed to the presence of hydrocarbon-degrading bacteria (Raymond et al., 1975). A program designed to investigate the potential for biodegradation of the gasoline by these organisms was then initiated. A laboratory study indicated that supplements of air, inorganic nitrogen, and phosphate salts could increase the numbers of hydrocarbon-degrading bacteria by one thousand-fold (Raymond et al., 1976). Small scale field studies also indicated that nutrient additions would enhance the growth of bacteria that degrade hydrocarbons (Jamison et al., 1975). A full scale program to stimulate the biodegradation of the gasoline in the aquifer was then initiated (Raymond et al., 1976). The nutrient amendment, which contained ammonium sulfate, disodium phosphate, and monosodium phosphate, was injected into the aquifer as a 30 percent concentrate by batch addition. Either ammonium or nitrate could serve as the nitrogen source. Magnesium, calcium, and iron were not included in the concentrate because the small scale field study indicted that these inorganic nutrients were not limiting (Jamison et al., 1975). Biodegradation of 1 liter of gasoline was estimated to require 44 g of nitrogen, 22 g of phosphorus, and 730 g of oxygen. However, Baehr and Corpcioglu (1985) estimated that degradation of a pound (0.63 liter) of gasoline requires 3.5 g of oxygen. Batch addition of the nutrients worked as well as continuous addition and was more cost-effective; however, high concentrations of nutrients may osmotically shock the microorganisms (Raymond et al., 1976). Oxygen was supplied by sparging air into the wells using paint sprayer-type compressors and Carboundum diffusers with a flow rate of 0.06 m^3/min. As a result, the bacterial population increased from about 10^3 to 10^7 cells/ml. High bacterial counts mirrored locations of high gasoline concentrations at the site (Raymond et al., 1975).

During the biostimulation program at the Ambler, Pennsylvania site, 32 cultures of bacteria that actively metabolized gasoline were isolated and characterized; the isolates included species of the genera Nocardia, Micrococcus, Acinetobacter, Flavobacterium, and Pseudomonas; some cultures could not be identified. Studies were conducted to determine the metabolic capabilities of these isolates (Jamison et al., 1976). The data suggested that the Nocardia cultures were largely responsible for the degradation of the aliphatic hydrocarbons whereas those from the genus, Pseudomonas, degraded the aromatics. Branched paraffins, olefins, or cyclic alkanes did not support the growth of any isolate. Co-oxidation may have played a major role in the biodegradation of these organics. An alternative hypothesis is that the bacteria capable of degrading these compounds were not isolated. The lack of microbial growth on some types of hydrocarbons may result from the toxicity or structure of the substrate. Straight chain aliphatics which are less than 10 carbons in length can be toxic whereas longer chains and branched alkanes are often resistant to microbial attack (Suflita, 1985). Substitutions on aromatics that are biodegradable may render them recalcitrant. Huddleston et al. (1986) gave the following order for petroleum hydrocarbon constituents, in order of decreasing biodegradability: linear alkanes C_{10-19}, gases C_{2-4}, alkenes C_{5-9}, branched alkenes C_{12}, alkenes C_{3-11}, branched alkenes, aromatics, and cycloalkanes.

The bioreclamation program conducted by Suntech at Ambler, Pennsylvania,was reasonably successful. During the period of nutrient addition, the concentration of gasoline in the ground water did not decline; however gasoline could not be detected in ground water 10 months later (Raymond et al., 1976). A thousand-fold increase in the numbers of total and hydrocarbon-degrading bacteria was observed in ground water from many wells (Raymond et

al., 1975). The waters from some wells exhibited foaming because of high microbial numbers and associated exopolysaccharides. Counts of microorganisms determined one year after nutrient addition was terminated indicated that the microbial population had declined. Estimates based on the amount of nitrogen and phosphorus removed from the nutrient solution suggested that between 88,600 and 112,400 L of gasoline were degraded. However, this estimate was not particularly accurate because some of the nutrients may have been adsorbed by soil or lost from the biostimulation area by dilution. In addition, the estimates were based on discrete samples rather than composited samples. Large quantities of nutrients were used in this project; approximately 79 metric tons of food grade reagents were purchased.

Steps in the biostimulation process--The Ambler, Pennsylvania site case history is an example of the biostimulation process. The basic steps involved in an in situ biorestoration program are the following: 1) site investigation; 2) free product recovery; 3) microbial degradation enhancement study; 4) system design; 5) operation; and 6) monitoring (Lee and Ward, 1986). The first step in the process is to define the hydrogeology and the extent of contamination of the site. Important hydrogeologic characteristics include the direction and rate of ground water flow, the depths to the water table and to the contaminated zone, the specific yield of the aquifer, and the heterogeneity of the soil. In addition, hydraulic connections between aquifers, potential recharge and discharge areas, and fluctuations in the water table must be considered. The sustainable pumping rate must also be determined (Roux, 1985; Brown et al., 1985a). These parameters can be determined by surveying the existing data for that site and region, reconnaissance by experienced hydrogeologists, geophysical surveys, excavation of test pits, and installation of boreholes and monitoring wells (Josephson, 1983). Low dissolved oxygen concentrations may indicate an active zone of hydrocarbon biodegradation (Chaffee and Weimer, 1983). The types and concentrations of contaminants is also important (Brown et al., 1985a). The type of remedial action chosen depends on the time elapsed since the spill, the areal extent of contamination, the nature of contaminants and whether the contamination is acute, chronic, or periodic. The urgency for action and the treatment level that must be achieved will depend on the potential for contamination of drinking water or agricultural water wells.

After defining the site hydrogeology, the next step is recovery of free product. Depending on the characteristics of the aquifer and contaminants, free product can account for as much as 91 percent of the spilled hydrocarbon (Brown et al., 1985a). The remaining hydrocarbon, which is sorbed to the soil and dissolved in the ground water, may account for 9 to 40 percent of the total hydrocarbon spilled; the majority is usually sorbed, however, the dissolved phase is the most difficult to treat. The pure product can be removed using techniques described in sections II B.2. an D. Physical recovery often accounts for only 30 to 60 percent of the spilled hydrocarbon before yields decline (Yaniga and Mulry, 1985).

Prior to in situ treatment, a laboratory study is conducted to determine the nutrient requirements that will enable the indigenous microorganisms to efficiently degrade the contaminants (Lee and Ward, 1985b). Kaufman (1986) suggested that these laboratory studies can provide a reliable basis for field trials; however, the studies must be performed under conditions that simulate the field. For example, Kuhlmeier and Sunderland (1986) conducted a laboratory investigation of the unsaturated zone using samples saturated with ground water. Clearly, the results of their study do not represent the fate of the organics in the unsaturated zone. A chemical analysis of the ground water provides little information about the nutrient requirements of the microflora (Raymond et al., 1978). However, the chemistry of the site will affect the nutrient formulation. For example, large quantities of oxygen may be consumed to oxidize reduced iron (Hallberg and Martinell, 1976). In addition, nutrients may sorb onto soils, especially silts and clays and be unavailable to the microflora (Brubaker and Crockett, 1986). Limestone and high mineral content soils and ground waters will also affect nutrient availability by reacting with the phosphorus.

Nutrient requirements are usually site specific. Nitrogen and phosphorus were required at the Ambler site (Raymond et al., 1976a); however, the addition of ammonium sulfate, mono-and disodium phosphate, magnesium sulfate, sodium carbonate, calcium chloride, manganese sulfate, and ferrous sulfate was required at other sites (Raymond et al., 1978; Minugh et al., 1983). The form of the nutrient may also be important; ammonium nitrate was less efficient than ammonium sulfate in one aquifer system.

Laboratory studies conducted to determine appropriate nutrient formulations can be performed using a number of techniques. An increase in the number of total and hydrocarbon degrading bacteria has been used to identify limiting nutrients in a factorial experimental design (Raymond et al., 1976, 1978). However, an increase in microbial numbers does not demonstrate that the substrate of interest is being used. Batch culture techniques designed to measure the disappearance of the contaminant (Flathman and Githens, 1985) and electrolytic respirometer studies designed to measure the uptake of oxygen also have been used (Flathman et al., 1985). The results of another laboratory investigation indicated that dissolved oxygen was the primary factor limiting biodegradation of aromatic contaminants at a wood creosoting site rather than inorganic nutrients (Lee, 1986). Biotransformation studies which measure the disappearance of the contaminants or mineralization studies which indicate the complete destruction of the compound to carbon dioxide and water will confirm that the contaminants are being degraded. Controls to detect abiotic transformation of the pollutants and tests to detect toxic effects of the contaminants on the microflora should be included (Flathman et al., 1984).

A system for injection of nutrients into the formation and circulation through the contaminated portion of the aquifer must be designed and constructed (Lee and Ward, 1985b). The system usually includes injection and production wells and equipment for the addition and mixing of the nutrient solution (Raymond, 1978). A typical system is shown in Figure 2-1. Placement of injection and production wells may be restricted by the presence of physical structures. Wells should be screened to accommodate seasonal fluctuations in the level of the water table. Air can be supplied with carborundum diffusers (Raymond et al., 1975), by smaller diffusers constructed from a short piece of DuPont Viaflo tubing (Raymond et al., 1978), or by diffusers spaced along air lines buried in the injection lines (Minugh et al., 1983). The size of the compressor and the number of diffusers are determined by the extent of contamination and the time allowed for treatment (Raymond, 1978). Nutrients also can be circulated using an infiltration gallery (Figure 2-2); this method provides an additional advantage of treating the residual gasoline that may be trapped in the pore spaces of the unsaturated zone (Brenoel and Brown, 1985). Oxygen also can be supplied using hydrogen peroxide, ozone, or soil venting (see section on alternative oxygen sources). Well installation should be performed under the direction of a hydrogeologist to ensure adequate circulation of the ground water (Lee and Ward, 1985b). Produced water can be recycled to recirculate unused nutrients, avoid disposal of potentially contaminated ground water, and avoid the need for makeup water.

Inorganic nutrients can be added to the subsurface once the system is constructed. Continuous injection of the nutrient solution is labor intensive but provides a more constant nutrient supply than a discontinuous process. Continuous addition of oxygen is recommended because the oxygen is likely to be a limiting factor in hydrocarbon degradation.

The performance of the system and proper distribution of the nutrients can be monitored by measuring the organic, inorganic, and bacterial levels (Lee and Ward, 1985b). Carbon dioxide levels are also an indicator of microbial activity in the formation (Jhaveri and Mazzacca, 1985). Depending on the charcteristics of the nutrients and soil, nutrients can be removed from solution by sorption onto soil (Brubaker and Crockett, 1986). About 90 percent of the ammonium and phosphate and 70 percent of the hydrogen peroxide added to a sandy soil with low calcium, magnesium, and iron was recovered. After passage of a nutrient solution through a column packed with a clay soil that had high calcium and magnesium but low iron and chloride levels, 100, 66 and 25 percent of the ammonium, phosphate, and hydrogen peroxide were recovered, respectively. However, after passage of a nutrient solution through a column packed with a clay soil high in calcium, magnesium, and chloride, but low in iron, 75, 100, and 15 percent of the ammonium, phosphate, and hydrogen peroxide, respectively, were recovered. Both soil and ground water samples should be collected and analyzed to fully evaluate the treatment effectiveness (Roux, 1985). Raymond et al. (1975) reported that the most difficult problem in optimizing microbial growth in the Ambler reservoir was the distribution of nutrients, which was made difficult by the heterogeneity of the dolomite formation.

Additional case histories in which oxygen was supplied by air sparging--In situ biorestoration has been largely used to treat gasoline spills and with reasonably good success. However, many of the reports on in situ biorestoration lack sufficient data to fully judge the overall effectiveness and costs associated with the process.
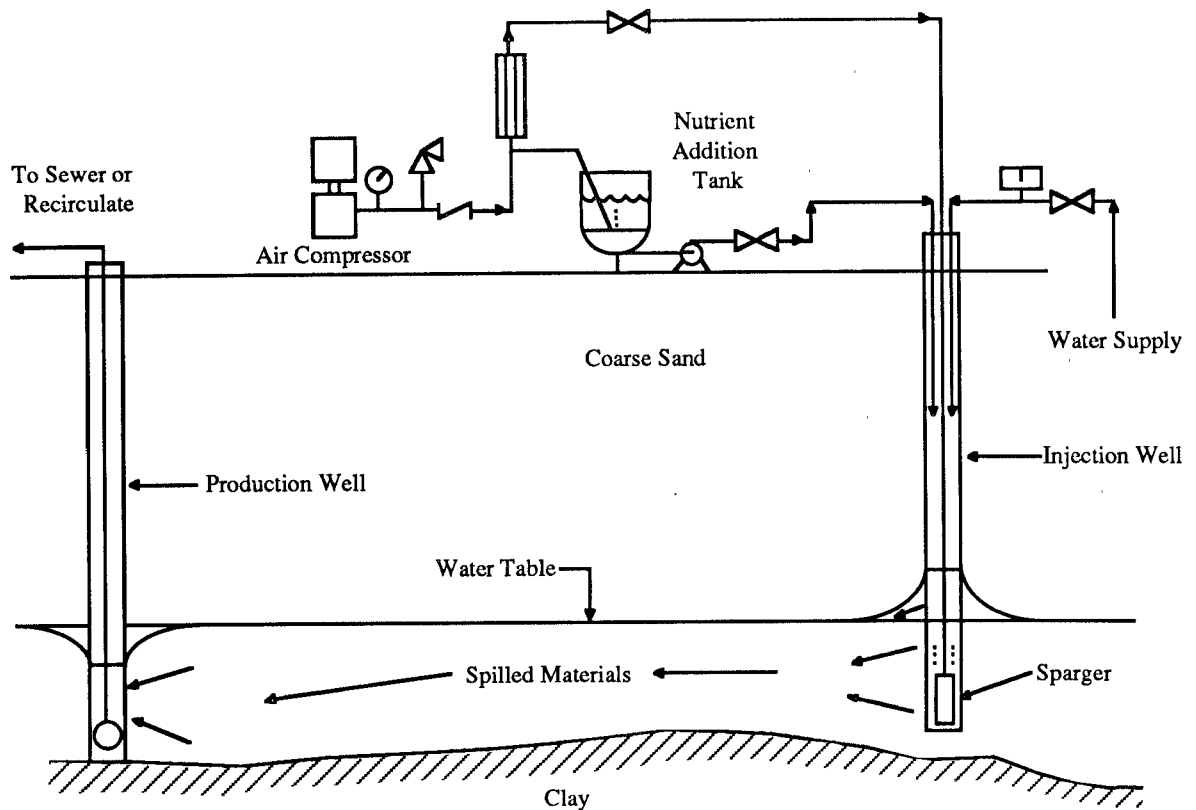
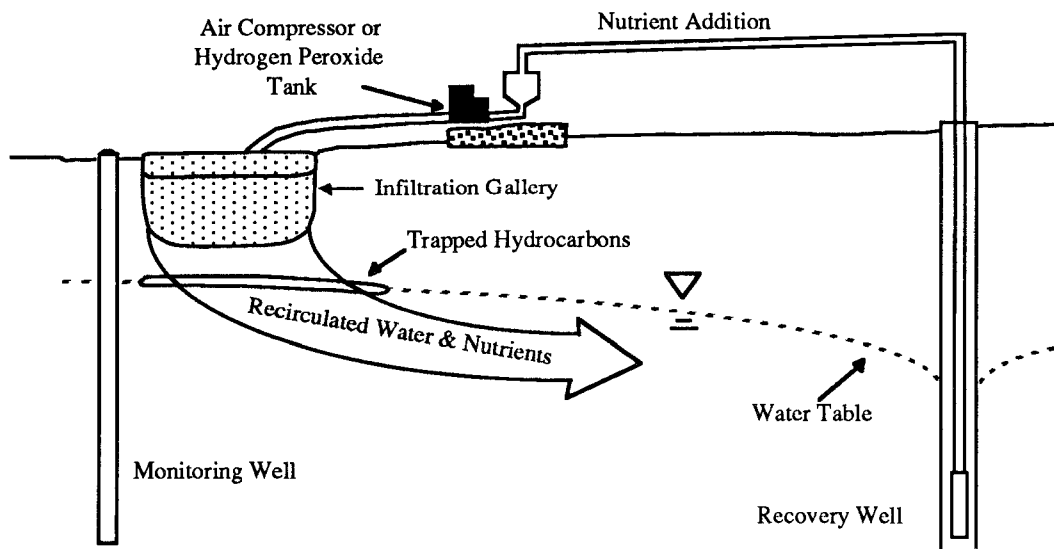Figure 2-1. Typical schematic for aerobic subsurface biorestoration.

Figure 2-2. Use of infiltration gallery for recirculation of water and nutrients in in situ biorestoration.

33

In a high permeability sand aquifer contaminated with hydrocarbons in Millville, New Jersey, the in situ biorestoration program was successful in removing free product, but residual hydrocarbon was found at the last sampling period (Raymond et al., 1978). The nutrient solution was moved through the formation at rates of 8 to 14 ft/day, but dissolved oxygen was rapidly consumed and did not increase in some of the main wells at all. However, analysis of core material collected from the aquifer indicated that the concentration of gasoline had not changed substantially during the biostimulation program. During the initial treatment process, inadequate dissolved oxygen levels led to the microbial formation of phenol, but the phenol levels declined as more aerobic conditions were achieved. A ten to one thousand-fold increase in the number of gasoline-utilizing bacteria was noted in the area with the highest gasoline levels. The cleanup met the state requirement of removal of the free gasoline and was subsequently stopped.

At a gasoline spill in La Grange, Oregon, nine months of treatment by in situ biorestoration and a vapor elimination program succeeded in removing the free product and mitigating the vapor problems at two restaurants (Minugh et al., 1983); however, the concentration of gasoline in the pits in the biorestoration treatment area still ranged from 100 to 500 ppm in the majority of the samples. After an additional three months of treatment, the dissolved organic levels in the ground water had decreased from an average of 20 ppm to less than 5 ppm in the majority of the samples.

Fumes released from a pipeline spill of gasoline temporarily closed an elementary school (Suntech, 1978). A pumping well was used to maintain the water table below the school's foundation and physical recovery was used to remove two-thirds of the gasoline. An enhanced biodegradation program was initiated by circulating nutrients and oxygen through the formation for six months. After the cleanup, hydrocarbons could not be detected and the fumes that had threatened the school had been eliminated.

Minimum hydrocarbon concentrations achievable by in situ biostimulation-The minimum concentration of hydrocarbon that can be achieved by in situ biorestoration is unknown and is most likely site specific. A natural gradient field test in a sandy Canadian aquifer required 434 days to reduce 1,000 to 2,400 ppb of benzene, toluene, and the xylene isomers to below the detection limits (1 to 2 ppb) in the absence of added nutrients and oxygen (Barker and Patrick, 1986). The distribution of dissolved oxygen in the plume was heterogeneous and probably controlled biodegradation of the aromatics.

Jensen et al. (1986) suggested that the indigenous microflora should be able to reduce the concentration of hydrocarbons below 1 mg/L when the initial hydrocarbon concentration is less than 10 mg/L and adequate quantities of nutrients and oxygen are supplied. The results of batch experiments using ground water from hydrocarbon-contaminated aquifers showed that the native microflora could generally reduce the concentrations of toluene, benzene, xylene, trimethyl benzene, naphthalene, methyl naphthalene, biphenyl, ethyl naphthalene, and dimethyl naphthalene from a range of 400 to 1,100 mg/L to less than 1 mg/L within a week in the presence of oxygen and nutrients; however, phenanthrene and toluene persisted at higher concentrations in two of the ground waters after incubation for six days.

The concentration of trace level organics in an aquifer may be reduced by providing a primary substrate that supports microbial growth and allows the organisms to act upon the trace level organics as secondary substrates (Bouwer, 1984). The concentration of the trace organic or secondary substrate is thought to be below the minimum substrate concentration (S_{min}) required to support microbial growth (Rittman and Kobayashi, 1982). The S_{min} concept was developed to describe limitations related to transport of organics into a biofilm and the subsequent kinetics of reaction. There are several examples of S_{min}. A reactor fed laboratory grade water containing 0.59 mg/L TOC was able to reduce acetate below the S_{min} value (0.03 mg/L) for acetate. Shimp and Pfaender (1985) demonstrated that addition of fatty acids, carbohydrates and amino acids enhanced the ability of mixed microbial populations to degrade substituted phenols. These data suggest that the addition of naturally occurring substrates may enhance the biodegradation potential of some xenobiotics. However, the addition of a primary substrate may not support the removal of some compounds. A biofilm supported by thymine could utilize alanine and acetate, both common metabolites, but not phenol and galactose (Rittman and Kobayashi, 1982).

34

Treatment trains--In many hydrogeologic systems which become contaminated from leaking underground storage tanks, a remediation process may be so complex in terms of contaminant behavior and site characteristics that no one system or unit will meet all requirements. Very often, it is necessary to combine several unit operations, in series and sometimes in parallel, into one treatment process train in order to effectively restore ground water quality to a required level (Wilson et al., 1986). Examples of treatment trains include:

(1) physical containment with product removal and surface treatment;
(2) product removal with unsaturated zone flushing followed by in situ chemical treatment;
(3) physical containment with in situ physical/chemical treatment; and
(4) product removal followed by in situ biological treatment.

Physical containment through barriers and hydrodynamic controls alone merely act as temporary plume control measures. However, hydrodynamic processes must also be integral parts of any withdrawal and treatment or in situ treatment measures. Most remediation projects where enhanced biorestoration has been applied have started by removing heavily contaminated soils. This was usually followed by installing pumping systems to remove free product floating on the ground water, before biorestoration enhancement measures were initiated to degrade the more diluted portions of the plume.

There are numerous proven surface treatment processes available for treating a variety of organic and inorganic wastewaters. However, regardless of the source of ground water contamination and the remediation measures anticipated, the limiting factor is getting the contaminated subsurface material to the treatment unit or units, or in the case of in situ processes, getting the treatment process to the contaminated material. The key to success is a thorough understanding of the hydrogeologic and geochemical characteristics of the area. Such an understanding will permit full optimization of all possible remedial actions, maximum predictability of remediation effectiveness, minimal remediation costs, and more reliable cost estimates (Wilson et al., 1986).

The role of biorestoration in combination treatment schemes is often difficult to assess. Yaniga et al. (1985a) described the cleanup of a gasoline spill in which an air stripper was used to reduce the contaminants in the withdrawn ground water and to supply oxygen before the water was recirculated to the aquifer via an infiltration gallery. Before recirculation, ammonium chloride, sodium monophosphate, sodium diphosphate, iron sulfate, and manganese sulfate were added in slug batches to the treated water. Additional oxygen was supplied by sparging air into the wells. As a result, the dissolved oxygen increased from a range of 0-5 to 5-10 ppm; the hydrocarbon degrading bacteria increased from 10^2-10^3 to 10^3-10^4 cells/ml with just oxygen addition by air stripping and sparging and then increased to 10^6 cells/ml with nutrient addition and additional oxygen. Brown et al. (1985b) identified another gasoline contaminated aquifer which was treated using air sparging. An estimated 25,000 to 30,000 gallons of gasoline entered a 20 ft thick coarse grain sand and fine gravel aquifer. Recovery of free product accounted for 18,500 gallons of the spilled gasoline; however, an estimated 10,000 gallons was sorbed to the soil at concentrations of 2,000 to 3,000 ppm and 30 to 40 ppm was dissolved in the ground water. The concentration of gasoline was reduced to less than 50 ppm in the soil and less than 1 ppm in the ground water by air sparging. Only 1 to 2 ppm of dissolved oxygen could be achieved in the wells by air sparging.

A spill of four solvents--methylene chloride, n-butanol, acetone, and dimethyl aniline--into a glacial till aquifer was withdrawn and treated by an activated sludge process, allowed to settle, and then recharged into the subsurface through injection trenches after being aerated and amended with nutrients (Jhaveri and Mazzacca, 1983). The recharge water contained organisms acclimated to the solvents in addition to a nutrient amendment containing nitrogen, phosphate, magnesium, sulfate, carbonate, manganese, and iron. Additional oxygen was supplied to the aquifer using a series of injection wells. Removal efficiencies of methylene chloride, n-butanol, and acetone were greater than 97 percent and the dimethyl aniline levels were reduced by greater than 93 percent in the above ground treatment. The concentrations of the solvents in the resulting effluent decreased to 0.04 mg/L for n-butanol, 0.92 mg/L for methylene chloride, 0.18 mg/L for dimethyl aniline, and 1.12 mg/L for acetone from initial concentrations of 19.1, 58.5, 2.9, and 38.8 mg/L, respectively. Based upon COD and gas chromatography analysis, the plume was reduced in size by 90 percent after three years of operation (Jhaveri and Mazzacca, 1985). The COD was reduced from 300 to 20 mg/L in one monitoring well. Based on the rate of ground water flow, this reduction in COD coincided with the expected arrival time of the treated ground water at that well. Elevated

35

levels of carbon dioxide in ground water collected from the treatment zones, in comparison to those observed in uncontaminated and decontaminated wells, suggested that in situ biorestoration was occurring. However, the solvents were detected in the ground water beyond the projected date for completion of the project and the New Jersey Department of Environmental Protection standards had not been achieved after three years of operation.

Flathman et al. (1985) and Quince et al. (1985) discussed cleanup of a methylene chloride spill using physical and biological above-ground treatment processes and in situ biological treatment. Following sand filtration to remove particulates, air stripping, combined with a heat exchanger to improve stripping efficiency, was initially used to treat the withdrawn ground water and the water was used to flush the soil (Quince et al., 1985). Air stripping removed about 98 to 99.9 percent of the methylene chloride in the withdrawn water. The concentration of methylene chloride in the ground water was reduced by 97 percent in one downstream monitoring well. Biological treatment was used to further reduce the concentration of the methylene chloride after addition of ammonia and phosphate. An activated sludge unit was seeded with acclimated organisms from a wastewater treatment plant receiving methylene chloride and these organisms were used to inoculate the soil (Flathman et al. 1985). After 43 days of in situ biological treatment, the concentration of methylene chloride in ground water from a monitoring well 20 ft from the spill declined from 192 to 6 ppm and 156 ppm chloride was released; however, it could not be determined whether the added bacteria or indigenous microflora or both were involved in methylene chloride degradation. Both air stripping and biological treatment removed 99.9 percent of the initial amount of methylene chloride present during the four months of field operation. The concentration of methylene chloride was reduced from 20,000 to less than 1 ppm in the source wells (Quince et al., 1985).

The subsurface at the Naval Air Engineering Center in Lakehurst, New Jersey, was contaminated with ethylene glycol resulting from the loss of about 4,000 gallons of cooling water from a lined surface storage lagoon (Flathman et al., 1984). The unsaturated zone was contaminated with concentrations of ethylene glycol as high as 4,900 mg/kg soil whereas ethylene glycol in the ground water was 2,100 mg/L. The highly contaminated soils were treated using injection and recovery wells whereas the ground water contaminated with ethylene glycol was treated by an above ground activated sludge unit and by adding ethylene glycol degrading bacteria and nutrients to the subsurface (Flathman et al., 1985). A biofeasibility study using an electolytic respirometer had demonstrated that the concentration of ethylene glycol could be reduced to less than 50 ppm within ten days by the natural microflora in the ground water and that the concentration of ethylene glycol at 1,300 ppm was not toxic. The initial operational phase was designed to degrade as much of the ethylene glycol as possible by treatment above ground with an activated sludge unit. The effluent from the activated sludge unit was amended with oxygen, nitrogen, and phosphorus, adjusted to neutral pH, and then reinjected into the subsurface to create a closed-loop system. The amended effluent was used to flush the contaminated soil and inoculate the ground water with nutrients and acclimated bacteria. The concentration of ethylene glycol in ground water collected from the plume recovery wells was reduced from 420-690 ppm to less than 50 ppm within 26 days (Flathman and Caplan, 1985); however, the unsaturated zone still contained pockets of ethylene glycol. A passive treatment system which involved adding lime and diammonium phosphate to the soil surface continued after termination of the active biorestoration phase. By the end of the treatment program, ethylene glycol could not be detected (detection limit, 50 ppm) in ground water collected from the production wells.

A shallow basin comprised of sand and pea gravel was contaminated with isopropanol and tetrahydrofuran (Flathman and Githens, 1985). In addition to isopropanol and tetrahydrofuran, acetone was also detected in the ground water and believed to be a byproduct of isopropanol degradation. Remedial action consisted of a recovery system, an above ground biological reactor, and recharging the aquifer with the effluent from the reactor which created a closed-loop system. The effluent, which contained acclimated bacteria, was also amended with nutrients before reinjection into the subsurface. The soils were flushed with the treated ground water to remove sorbed organics and introduce acclimated organisms into the aquifer. Maximum concentrations of isopropanol (950 ppm) and acetone (190 ppm) were detected in ground water from a centrally located well as a result of flushing pockets of contamination from the subsurface. The pattern of change in isopropanol and acetone concentrations was similar. The concentration of acetone in the ground water increased initially until the majority of the isopropanol had been degraded, and then declined to less than 0.2 ppm. Extrapolations from the data indicated that 99 percent of the contaminants would be removed within 33 days. Estimated cost for removal and disposal of 200,000 ft³ of contaminated soil was $550,000 whereas the biological treatment program was estimated to cost one-fifth as much.

Winegardner and Quince (1984) documented two additional case histories of in situ biorestoration that involved addition of acclimated bacteria. The first case history described the cleanup of a train derailment which released a semi-soluble aliphatic hydrocarbon plasticizer. Recovery wells were used to collect the plasticizer from the subsurface. Later, surface recharge and shallow injection were used to flush the plasticizer out of the soil; this treatment reduced the peak concentration of greater than 2,000 ppm in a widespread area to a much smaller zone after 70 days, in addition to reducing the concentration of the plasticizer throughout the contaminated area. Air stripping and carbon adsorption were used initially; however, these techniques were replaced by biological treatment using activated sludge. The water treated by activated sludge was used as an inoculant to introduce the acclimated bacteria into the subsurface to enhance in situ biorestoration. The concentration of the plasticizer in the recovered water was reduced from approximately 1,700 to 400 ppm after clarification; however, the importance of each component in the treatment process could not be determined.

The second case history involved contamination of a glacial kame deposit of sand, gravel, silt, and clay with chloroform from a leaking pipeline. Ground water was withdrawn and treated with a mixed media prefilter, an activated sludge bioreactor and settling vessel, and a heated air stripper. The effluent from the activated sludge bioreactor was used as an inoculant for biorestoration. The effluent from the air stripper was discharged into a process sewer or into the subsurface. A forced flushing/recovery system was used to enhance the recovery of the chloroform. Biological treatment followed the physical recovery; however, treatment effectiveness was not discussed.

Alternate Oxygen Sources

The supply of dissolved oxygen may limit in situ biorestoration of hydrocarbons, especially in low permeability aquifers (Raymond et al., 1978). Depending upon the temperature of the ground water, only 8 to 12 mg/L of dissolved oxygen can be achieved by air sparging, and incomplete transfer of oxygen into water may reduce this even further. Using only the oxygen provided by sparging air into the ground water, 1,500 to 5,400 pore volumes of air would be required to completely degrade the hydrocarbon in an aquifer that is six feet deep, one acre in size, has a porosity of 30 percent, and contains 4000 mg/L gasoline (Brown et al., 1984).

Alternative sources of oxygen include pure oxygen, hydrogen peroxide, and ozone. Other methods of supplying oxygen to the subsurface are soil venting or air flooding (Wilson and Ward, 1986) and colloidal dispersions of air in a surfactant matrix (Michelsen et al., 1985). Concentrations of 40 to 50 mg/L of dissolved oxygen can be achieved with pure oxygen; however pure oxygen is somewhat expensive, may bubble out of solution before the microflora can use it, and is extremely flammable (Brown et al., 1984).

Hydrogen peroxide--Hydrogen peroxide, decomposes to form one molecule of water and half of a molecule of oxygen, and can be used as a source of oxygen (Equation 2-1).

$$H_2O_2 \rightarrow H_2O + 1/2\ O_2 \qquad\qquad (2\text{-}1)$$

However, hydrogen peroxide is used as a sterilant at concentrations of 3 percent and levels as low as 200 ppm can be toxic to microorganisms. Ground water organisms inoculated into sand columns could tolerate 0.05 percent hydrogen peroxide, but higher levels were toxic (Britton and Texas Research Institute, Inc., 1985) In a study designed to investigate the effect of increasing concentrations of hydrogen peroxide on gasoline degradation, the culture acclimated to hydrogen peroxide levels that were gradually increased from 0.05 to 0.2 percent; however, removal of gasoline was not greatly increased in comparison to the control without hydrogen peroxide. Microbial counts were higher in columns in which hydrogen peroxide was incrementally increased than those which received 0.05 percent hydrogen peroxide. These data suggest an oxygen limitation at lower concentrations of hydrogen peroxide. Large populations of microorganisms survived high hydrogen peroxide concentrations better than small populations (Texas Research Institute, 1982). In a column study in which oxygen concentration was varied from 8 to 200 ppm using air, 60 percent nitrogen/40 percent oxygen, pure oxygen, or a hydrogen peroxide solution, microbial growth and gasoline degradation were greater in columns amended with hydrogen peroxide which provided the highest concentration of available oxygen (Brown et al., 1984). At concentrations greater than 100 ppm, hydrogen peroxide may degas to form air bubbles and block some of the pores in the aquifer.

Decomposition of hydrogen peroxide may also be catalyzed by iron and fluctuations in pH (Britton and Texas Research Institute, Inc., 1985). In addition to comprising part of the nutrient formulation, certain forms of phosphate, such as potassium monophosphate, can be used to stabilize hydrogen peroxide solutions. To reduce phosphate adsorption by the soil, a combination of simple and complex polyphosphate salts can be used (Brown et al., 1986). Results from a field test in which hydrogen peroxide was used to increase the dissolved oxygen content of the ground water indicated an increase from 1 to 15 ppm within 70 hr at a monitoring well located 25 ft downgradient of the injection well.

Raymond et al. (1986) received a patent on a process for stimulating biodegradation of organic contaminants in the subsurface with hydrogen peroxide. The patent described several formulations of nutrient and hydrogen peroxide solutions and processes that can stabilize the decomposition of hydrogen peroxide, control movement of the solution through the aquifer, remove metal ions from the subsurface which catalyze hydrogen peroxide decomposition, and disrupt biofilms that form at the point of injection. Hydrogen peroxide decomposition can be controlled by the addition of peroxidase, oxidase, or a transition metal (iron, copper, manganese, chromium, or other material including the chelated forms of these metals). In addition, condensed phosphates can be perfused into the aquifer to deactivate or remove substances that catalyze hydrogen peroxide decomposition.

Movement of the hydrogen peroxide solution through the formation can be controlled by hydratable polymeric materials, interface modifiers, and densifiers (Raymond et al, 1986). The hydratable polymeric materials, such as polysaccharides, polyacrylamides, and polyacrylamide copolymers, increase the viscosity of the solution. An increase in viscosity reduces the rate of diffusion and slows the movement of the solution. The addition of surfactants will decrease the interfacial tension, prevent clays from swelling, disperse materials throughout the zone of contamination, and decrease the metal-catalyzed decomposition of hydrogen peroxide. For example, the zone of treatment can be extended into the capillary zone by adding soluble orthophosphoric salts and condensed phosphoric acids to increase the capillary rise of the aqueous solution. Salts, such as sodium chloride, calcium chloride, and sodium bromide, can be used to change the density of the nutrient solution. Biofouling can be controlled by adding high concentrations (0.5 to 3%) of hydrogen peroxide; the effectiveness of hydrogen peroxide in controlling biofouling may be enhanced by the addition of dilute acid.

Hydrogen peroxide has been used to enhance oxygen supply in the subsurface in many remedial programs. In most cases, the additional oxygen was required to degrade hydrocarbons in aquifers contaminated from gasoline spills. One case study involved the contamination of a relatively impermeable soil (ground water movement, 2 to 3 ft/year) with gasoline (Yaniga and Mulry, 1984). About 50 to 60 percent of the free product was recovered; however, concentrations of hydrocarbon in the range of 3,700 to 7,200 ppm remained sorbed to the soil. A feasibility study was conducted to identify an in situ microbial population capable of degrading the hydrocarbons when supplied with nutrients and oxygen. Hydrogen peroxide was used as the source of oxygen. After two months of operation, free product recovery reached a maximum of 25 to 30 gal/day, numbers of hydrocarbon-degrading bacteria increased one to three orders of magnitude, and the concentration of sorbed product fell to a range of 2300 to 2900 ppm.

In another in situ biorestoration program designed to clean up gasoline from a leaking underground storage tank, oxygen was initially supplied by air stripping and sparging and then by hydrogen peroxide. A layer of heavy silt loam which was underlaid by a layer of fractured shale and silt stone was contaminated by the spill (Yaniga, 1982). The gasoline infiltrated into the ground water and the resulting plume, containing dissolved hydrocarbons, contaminated 12 domestic water wells with concentrations ranging from less than 10 ppb to 15 ppm. Ground water was withdrawn and an air stripper was used to remove volatile organics and add oxygen; the oxygenated water was then recirculated into an infiltration gallery to facilitate removal of the trapped organics. Air stripping reduced the dissolved organics to less than 0.1 ppm. Additional oxygen was introduced by sparging air through the 20 to 30 foot water column in the wells. The initial dissolved oxygen levels in the contaminated zone were 0-1 mg/L, whereas those in the uncontaminated wells were 7-9 mg/L. Dissolved oxygen levels rapidly increased in the periphery of the plume; after six weeks of air sparging, the concentration of dissolved oxygen increased to 3-5 mg/L in the contaminated zone. The nutrient solution included ammonium chloride, sodium phosphate, and various mineral salts. Existing monitoring wells were used to add the nutrients because nutrient diffusion was slower than desired. In the first 20 months of treatment, reductions of 50 to 85 percent of the dissolved

38

hydrocarbons were achieved; however, treatment was continued because significant levels of hydrocarbon remained. After this treatment period, reductions in the concentrations of dissolved hydrocarbons were minimal and believed to be a result of inadequate oxygen supply (Brown et al., 1986); in addition, a biofilm had developed and plugged the injection wells (Yaniga et al., 1985b).

To increase the concentration of dissolved oxygen, a trial experiment using hydrogen peroxide was conducted in which 5 gallons of 100 ppm hydrogen peroxide was added to an injection well 40 ft from a pumping well (Yaniga et al., 1985b). As a result, the dissolved oxygen content in the ground water collected from the pumping well increased from 0.5 to 8 ppm in 24 hr with a concommitant increase in microbial activity. The decision was then made to add 100 ppm hydrogen peroxide to the infiltration gallery and to the injection wells to increase the concentration of dissolved oxygen in the formation. Addition of hydrogen peroxide also controlled growth of the biofilm on the screens of the injection wells. After addition of hydrogen peroxide, the concentration of hydrocarbons in the ground water had been reduced from 15 to 2.5 ppm. Continuation of this treatment removed the dissolved hydrocarbons in ground water from eight of the 12 wells. Between 200 and 1,200 ppb remained in the other four wells (Brown et al., 1986).

Hydrogen peroxide-assisted biodegradation followed by granular activated carbon polishing was used to treat a spill of waste solvents and fuel (Brenoel and Brown, 1985; Westray et al., 1985). The source of the contamination was an excavated area around several leaking tanks at a laboratory facility. The fill material and soil surrounding the storage tanks was contaminated with 1000 to 3000 ppm hydrocarbon. The hydrocarbon was composed of xylenes, benzene, toluene, ethyl benzene, C_4-C_{12} alkanes, and C_7-C_{10} alkanes. About 2,600 L of free product was recovered using a sump pump; however, an estimated 1,100 to 3,400 L of the hydrocarbon remained. The subsurface consisted of sand and sandy clay with ground water flows in the hundreds of feet per year. The total number of bacteria in the well water ranged from 300,000 to 420,000 cells/ml; hydrocarbon degraders ranged from 5,400 to 6,100 cells/ml. Carbon adsorption and enhanced bioreclamation were considered for remedial action. Carbon adsorption was estimated to require 10 to 20 years and cost $470,000 to $850,000 whereas enhanced bioreclamation was estimated to require four to eight months and cost $180,000 to $270,000 (Brown et al., 1986). Enhanced bioreclamation was chosen and the process design consisted of four injection wells and a pumping well with flows of 15 to 25 gpm (Westray et al., 1985). A nutrient solution consisting of ammonium chloride and sodium phosphates was injected by batch addition. Hydrogen peroxide was injected continuously following a short period during which only nutrients were added; addition of nutrients without oxygen had little effect because of the initial low dissolved oxygen content (0.8 ppm). After 72 days, 1,200 pounds of nutrients and 250 gallons of the hydrogen peroxide solution had been added. The number of hydrocarbon degrading microorganisms increased 130 fold and the concentration of dissolved oxygen in the ground water increased to 10.5 ppm after the biorestoration program was initiated. The concentration of hydrocarbon decreased from 22,700 to 581 ppb in 44 days and to non-detectable levels in one monitoring well after 72 days. Elevated concentrations of contaminants detected in another monitoring well were thought to result from a leaking line. An estimated 150 to 400 gallons of the mixed fuels and solvents had been degraded (Brown et al., 1986). However, the formation became partially clogged after 72 days of operation. Clogging of the formation may have resulted from the movement of silt and degradation of the cement that lined the storage tank vault (Brenoel and Brown, 1985). An activated carbon system was then used as a polishing step to reduce the hydrocarbon concentration below 10 ppb in the tank vault and soil.

The cost for a 6 to 18 month bioreclamation program at the laboratory facility was estimated between $180,000 and $270,000 (Brown et al., 1986). Estimates were $50,000 to $75,000 to start the bioreclamation process and $130,000 to $220,000 for services and nutrients. The cost for excavation was estimated between $600,000 and $1,500,000, and the program was projected to take less than six months; however, facilities on the site would restrict excavation. Withdrawal and treatment by carbon absorption was estimated to cost $470,000 to $850,000 and require 10 to 20 years because of limited extractability of the contaminants.

A less successful demonstration of enhanced bioreclamation using hydrogen peroxide was reported by Brown and Norris (1986). A formation consisting of silt, sand, and gravel deposits was contaminated by a spill of 80,000 gal of unleaded gasoline. Two subsurface zones were identified in the test area: 1) a fine quartz sand with some limestone and dolomite grains and ferro-magnesium minerals with traces of limonite and pebbles of dolomite,

limestone, and granite and 2) another zone of fine quartz sand with large amounts of fines and silt which impeded ground water flow. The hydraulic conductivity ranged between 8.8 to 15.2 x 10^{-4} cm/sec. A free product recovery program was implemented; however, between 300 and 10,000 ppm of hydrocarbon remained in the soil and 50 to 60 ppm remained in the ground water after five years. The concentration of total hydrocarbons in the cores averaged 5,477 ppm with a range of 4,823 to 6,331 ppm for several groups. The highest concentrations were detected at the water table at depths of 24 to 26 ft. The treatment zone was estimated to contain 16,500 % 6,700 (std. dev.) pounds of gasoline. Ambient nutrient levels in the ground water were less than 1 ppm and the dissolved oxygen content was less than 0.4 ppm. Total counts and counts of hydrocarbon-degrading bacteria grown on nutrient agar were 1.2 x 10^3 and 2 x 10^2 cells/g, respectively. Biostimulation was tested in a section of the plume surrounded by two triangular patterns of monitoring wells which surrounded an inner infiltration gallery. Nutrients were batch fed to the inner gallery and then followed by addition of hydrogen peroxide solutions which were gradually increased from 0 to 500 ppm. Phosphorus levels reached 100 to 250 ppm in the inner gallery and ranged from 1 to 10 ppm outside the gallery. The concentration of nitrogen ranged from 100 to 250 ppm in the inner gallery and from 10 to 50 ppm outside of the gallery. Total bacterial counts reached 10^6 cells/ml in the inner gallery and 6.0 x 10^3 cells/ml outside of the gallery; gasoline-utilizers also increased.

The concentration of hydrocarbon in the soil was measured after 0, 32, 91 and 164 days during the test and at depths of 23, 25, 27, and 29 ft below the land surface (Brown and Norris, 1986). During the test, the concentration of hydrocarbon was reduced from 5,490 to 1,874 ppm (65%). Removal of hydrocarbons was highest (from 5,643 to 1,743 ppm) in the inner gallery near the injection area whereas a low permeability zone was less effectively treated because of reduced circulation of nutrients. In addition, the concentration of total hydrocarbons was reduced by 63 percent outside and between the galleries. The hydrocarbon concentration at the water table was reduced from 6,087 to 4,058 ppm; from 2,946 to 1,008 ppm immediately below the water table. The data indicate that substantial quantities of hydrocarbons remained adsorbed onto the soil after in situ biostimulation although more improvement may have occurred with continued treatment.

A field demonstration of in situ biorestoration using hydrogen peroxide in a very gravelly clay loam was adversely affected by the low permeability (3.9 x 10^{-5} to 3.3 x 10^{-3} cm/sec) of the soil (Lee et al., 1986). The heterogeneity of the soil and distribution of the contaminants made it difficult to inject nutrients and pump water. The contamination resulted from a disposal pit containing chromium sludges, electroplating wastes, chlorinated solvents, cresols, chlorobenzenes, and other compounds (Wetzel et al., 1985a; Wetzel et al., 1985b). The organic compounds that were identified included tetrachloroethylene, trichloroethylene, trans-1,2-dichloroethylene, and o- and p-dichlorobenzene. Heavy metals present at concentrations greater than 10 mg/L included antimony, chromium, copper, lead, nickel, and zinc and the concentrations of silver, cadium, and mercury were high in some locations (Wetzel et al., 1985a and Wetzel et al., 1985b). The formation consisted of gravel lenses and layers of fine grained soils with low hydraulic conductivities. The water table was perched, only 4 to 8 feet thick, and exhibited seasonal fluctuations. Direct microbial counts in soil ranged from 7.6 to 170 x 10^6 cells/g (wet weight); viable counts ranged from less than 100 to 7 x 10^6 cells/g on both rich and poor media. Laboratory studies conducted under aerobic conditions indicated that the chlorobenzenes, hydrocarbons, and aromatics could be biodegraded. Degradation of the organic contaminants separated by gas chromotography and thought to represent n-alkanes was faster in the aerated microcosms than in those supplied with hydrogen peroxide, which may indicate hydrogen peroxide toxicity. Unresolved hydrocarbons representing branched alkanes were removed under aerobic but not anaerobic conditions. The results from these microcosm studies suggested that biological degradation was feasible, but the heterogeneity of the subsurface and the contaminants present seriously limited application of the biorestoration process. The presence of heavy metals was not expected to prevent biodegradation, but the treatment process could induce metal mobilization.

The treatment system design for in situ biorestoration consisted of nine extraction and four injection wells that were connected to a central surge tank and a distribution box (Heyse et al., 1985). One upgradient and two downgradient wells were installed to monitor the influence of the treatment in untargeted areas. Nutrients were added two weeks before the hydrogen peroxide. After two months of treatment, the effectiveness of the treatment could not be determined because of a change in analytical methods; however, a number of problems were noted with the field demonstration. Hydrocarbon levels increased in the ground water for unknown reasons. In

addition, the nutrient solution precipitated initially when added on a continuous basis; the precipitation problem was reduced by switching to batch amendments. The temperature in the well water increased and fluctuated because the impermeable soil would not sustain flow adequate to prevent the pumps from overheating. Microbial numbers in the infiltration zone remained low, perhaps due to hydrogen peroxide toxicity. Antimony and lead may have been mobilized within the aquifer and the nutrients had not reached most of the wells at the time of this report (Science Application International Corporation, 1985).

Continued treatment for six months resulted in decreases in the levels of chlorobenzene and total hydrocarbons (Wetzel et al., 1986). The breakthrough of the nutrient solution was rapid in the highly permeable zones, but poor in the less permeable strata. Elevated concentrations of carbon dixoide were detected in the treatment zone which suggested an increase in microbial activity. However, the concentration of most of the organic compounds did not decline and biorestoration of the site was not successful.

Ozone--In addition to hydrogen peroxide, ozone (O_3) can be used as an alternate source of oxygen. Ozone was used in an in situ biorestoration program to remediate a hydrocarbon spill in a railroad yard in Karsruhe, West Germany (Nagel et al., 1982). The presence of organic contaminants in the drinking water wells for the city of Karlszruhe was traced to the hydrocarbon spill in the train yard. The concentration of organics, iron, and manganese in the ground water increased but the dissolved oxygen content decreased. The water was withdrawn, treated with 1 g of ozone/gram of dissolved organic carbon for four minutes and then reinjected into the formation through five infiltration wells at a rate of 80-120 m^3/hr. Supplemental nutrients were not added. The purified water formed a barrier to prevent further contamination of the withdrawal well. The ozone treatment increased the dissolved oxygen levels in the ground water which stimulated the microbial population and enhanced the degradation of the contaminants in the aquifer. The maximum efficiency of introducing dissolved oxygen into the ground water was 80 percent of the initial concentration of ozone. Oxygen consumption by the indigenous microbes reached approximately 40 kg/day. The dissolved organic carbon decreased from a range of 2.5 to 5.5 g/m^3 to a steady state value of slightly more than 1 g/m^3; little mineral oil hydrocarbons remained. The levels of iron and manganese were also reduced. Although the total number of bacterial cells increased, microbial counts on media which selected for disease-causing organisms did not increase. The removal of the hydrocarbons probably resulted from both in situ microbial activity and chemical oxidation by the ozone. Hydrocarbons could not be detected in the biostimulated section of the aquifer in water collected 1.5 years after treatment.

Soil venting--Soil venting or air flooding can be used to supply oxygen for in situ biorestoration. Organic vapors from the unsaturated zone are removed by increasing the flow of soil gases using vapor recovery wells and air inlet wells (Crow and Minugh, 1986). The volatile organic contaminants partition into the soil gas and are transported to the vapor recovery wells. The increase in soil gas flow in the unsaturated zone makes more oxygen available to reaerate the ground water. Wilson and Ward (1986) suggested that air flooding can be used to supply oxygen during in situ biorestoration. Air contains 20 times more oxygen than water and is less viscous. For a fine sand or silt, about 32,000 pore volumes of water in comparison to 4000 volumes of air is required to meet the oxygen demand for degradation of saturating concentrations of hydrocarbons. Fewer volumes of each is required for more porous soils. In addition to supplying oxygen, air flooding also removes vapors by physical weathering. In the absence of a layer of pure product floating on the water table, the water table can be lowered by withdrawing ground water to bring the contaminated region into the unsaturated zone for treatment. However, lowering the water table would produce large quantities of contaminated ground water that must be treated. Soil venting is currently being applied for in situ restoration of gasoline-contaminated soil by supplying oxygen to a 95 foot thick unsaturated zone where the contaminants are held (Kuhlmeier and Sunderland, 1986).

Collodial gas aphrons--Michelsen et al. (1985) suggested that a colloidal dispersion of air contained in a surfactant matrix could be used to supply oxygen for in situ bioreclamation. The microdispersion of air, known as colloidal gas aphrons, is prepared by passing air or pure oxygen through a venturi with a very small gas entry port into a surfactant solution or by use of a spinning disk apparatus. The resulting colloidal material is basically a suspension of fine soap bubbles with diameters of 25 to 50 microns that contain up to 65 percent gas. Up to about 55 percent of the pore space in sands can be filled with the colloidal air dispersion. Coarse sand was better than a fine sand in retaining the colloidal air. Laboratory tests indicate that the technique can support the aerobic metabolism of phenol and hexadecane; better removal of hexadecane was achieved when the suspension was

41

prepared with oxygen (90%) than air (70%). Methods for application of the colloidal air in the field are still in the devlopmental stages. In addition, biodegradation of the surfactants has also not been addressed.

Summary of Aerobic In Situ Biostimulation Processes

There are a number of advantages and disadvantages in using in situ biorestoration (Table 2-4). Compounds ranging from petroleum hydrocarbons to solvents have been treated by in situ biorestoration (Table 2-5). Unlike many aquifer remediation techniques, in situ bioreclamation can often treat contaminants that are sorbed to soil or trapped in pore spaces. In addition to treatment of the saturated zone, organics held in the unsaturated and capillary zone can be treated when an infiltration gallery or soil flushing is used. Biodegradation in the subsurface can be enhanced by increasing the concentration of dissolved oxygen, through the use of hydrogen peroxide, ozone, or a colloidal dispersion of air (colloidal gas asphrons). Complete biodegradation (mineralization) of organic compounds usually produces carbon dioxide, water, and an increase in cell mass. However, incomplete degradation (biotransformation) of organic materials can produce byproducts that are more toxic than the parent molecule. An example of biotransformation is the degradation of isopropanol to acetone at a hazardous waste site described by Flathman and Githens (1985). The levels of acetone increased initially, but declined after most of the isopropanol was removed. In situ biorestoration may rely on the biodegradation potential of the indigenous

Table 2-4. Advantages and Disadvantages of Biorestoration (J. R. B. Associates, 1982; Yang and Bye, 1979)

Advantages

● Can be used to treat hydrocarbons and certain organic compounds, especially water-soluble pollutants and low levels of other compounds that would be difficult to remove by other methods

● Environmentally sound because it does not usually generate waste products and typically results in complete degradation of the contaminants

● Utilizes the indigenous microbial flora and does not introduce potentially harmful organisms

● Fast, safe and generally economical

● Treatment moves with the ground water

● Good for short-term treatment of organic contaminated ground water

Disadvantages

● Can be inhibited by heavy metals and some organics

● Bacteria can plug the soil and reduce circulation

● Introduction of nutrients could adversely affect nearby surface waters

● Residues may cause taste and odor problems

● Labor and maintenance requirements may be high, especially for long term treatment

● Long term effects are unknown

● May not work for aquifers with low permeabilities that do not permit adequate circulation of nutrients

Table 2-5. Contaminants Treated By In Situ Biostimulation

Contaminants	Treatment Description	References
high octane gasoline	air sparging with nitrogen and phosphorus addition	Raymond et al., 1975 Raymond et al., 1975 Jamison et al., 1975 Jamison et al., 1976
gasoline	air sparging with complete mix of inorganics	Raymond et al., 1978
gasoline	air sparging with addition of complete inorganic nutrient solution	Minugh et al., 1983
gasoline	air sparging and addition of nutrients	Suntech, 1978
gasoline	dissolved oxygen supplied by an air stripper and sparging; nutrients also added	Yaniga et al., 1985a Yaniga et al., 1985b
gasoline	dissolved oxygen supplied by an air stripper	Brown et al., 1985b
gasoline	hydrogen peroxide plus nutrients	Yaniga and Mulry, 1984
gasoline	initial treatment utilized air stripping; hydrogen peroxide used later with the nutrient formulation	Yaniga, 1982 Brown et al., 1985b Yaniga et al., 1985b
unleaded gasoline	hydrogen peroxide supplied the oxygen	Brown and Norris, 1986
mineral oil hydrocarbons	withdrawn water treated with ozone and reinfiltrated	Nagel et al., 1982
gasoline	soil venting used to supply oxygen to unsaturated zone	Kuhlmeier and Sunderland, 1986

(Continued)

Table 2-5. (Continued)

Contaminants	Treatment Description	References
waste solvents and alkanes	nutrients plus hydrogen peroxide	Brown et al., 1985b Westray el al., 1985 Brenoel and Brown, 1985 Brown et al., 1986
methyl chloride, n-butanol, dimethyl aniline, acetone	withdrawal and treatment by an activated sludge process and recharge of aerated nutrient-laden water	Jhaveri and Mazzacca, 1983 Jhaveri and and acetone Mazzacca, 1985
methylene chloride	withdrawal and treatment with air stripping followed later by treatment in an activated sludge unit and recharge	Quince, et al., 1985 Flathman et al., 1985
ethylene glycol	treatment following withdrawal with ethylene-degrading bacteria and nutrients and then recharge	Flathman et al., 1985 Flathman and Caplan, 1985
isopropanol and tetrahydrofuran	treatment in an above ground reactor with addition of acclimated microbes to the aquifer along with nutrients	Flathman and Githens, 1985
aliphatic hydrocarbon plasticizer	activated sludge and recharge of acclimated bacteria and nutrients	Winegardner and Quince, 1984
chloroform	activated sludge bioreactor with the bacteria innoculated into the subsurface	Winegardner and Quince, 1984

subsurface microflora which usually contains few pathogenic organisms unless the aquifer has been contaminated with wastewaters (Keswick, 1984). The time required to treat subsurface pollution using in situ biorestoration can often be faster than some withdrawal and treatment procedures. A gasoline spill in Ambler, Pennsylvania, was remediated in 18 months using in situ biorestoration whereas pump and treat techniques were estimated to require 100 years to reduce the concentrations of gasoline to potable levels (Raymond et al., 1976). In situ biorestoration can also cost less than other remedial options. Flathman and Githens (1985) estimated that the cost of in situ biorestoration would be one-fifth of that for excavation and disposal of soil contaminated with isopropanol and

44

tetrahydrofuran and in addition would provide an ultimate disposal solution. The areal zone of treatment using biorestoration can be larger than other remedial technologies because the treatment moves with the plume and can reach areas which are otherwise inaccessible.

There are also disadvantages to in situ biorestoration programs. Many organic compounds in the subsurface are resistant to degradation. In situ biorestoration requires an acclimated population; however, adapted populations may not develop for recent spills or recalcitrant compounds. Heavy metals and toxic concentrations of organics may inhibit microbial activity and preclude the use of the indigenous microflora for in situ biorestoration at some sites. One option in this instance would be to remove the inhibitory substances and then seed the subsurface with appropriately adapted microorganisms; however, the benefits to adding microorganisms to the subsurface are still undemonstrated. The formation and injection wells may clog from profuse microbial growth which results from the addition of oxygen and nutrients. In one biostimulation project, microbial growth produced foaming in the well casings (Raymond et al., 1976a). In addition, the hydrodynamics of the restoration program must be properly managed. The nutrients added must be contained within the treatment zone because the profusion of inorganics into untargeted areas can result in eutrophication. High concentrations of nitrate can render ground water unpotable. Metabolites of partial degradation of organic compounds may impart objectionable tastes and odors. For example, the incomplete degradation of gasoline under low dissolved oxygen conditions resulted in phenol production; phenol was then degraded when more aerobic conditions were achieved (Raymond et al., 1978). Biostimulation projects require continuous monitoring and maintenance for successful treatment; whether these requirements are greater than those for other remedial actions is debatable. The process results in increased microbial biomass which could decompose and release undesirable metabolites. In addition, microbial growth can exert an oxygen demand that may drive the system anaerobic and result in the production of hydrogen sulfide or other objectionable byproducts. The long term effects of biorestoration are unknown. In situ biorestoration is difficult to implement in low permeability aquifers in which perfusion of nutrients and oxygen is slow or negligible; however, many in situ physical and chemical remediation processes are subject to the same restrictions. The success of in situ treatment schemes in low permeability aquifers depends on transporting the nutrients to the microflora or the active agent to the contaminants. The process has been used in different hydrogeological formations (Table 2-6).

Potential problems for any aquifer restoration program include reversible adsorption of the contaminants, poor delineation of the plume, inadequate sizing of the recovery system, pollution at depth, high costs, treating and disposing of large amounts of pollutants, constraints on ground water pumping, access to the contaminated area, and substantial quantities of pollutants in the vadose zone (Schmidt, 1983). To decrease the expense of an aquifer cleanup, Nyer (1985) advocated a policy of life cycle design for remedial actions in which some of the equipment could be recycled and used at other sites. An example of this system was proposed to remediate contaminated ground water from a Gulf Coast hazardous waste site. The ground water contained high concentrations of phenol and enough dissolved solids (15,000 mg/L) to be considered a brine. The treatment system consisted of two activated sludge units, a fixed film-activated sludge unit, a dual media filter, and a carbon adsorption column. The components of the treatment system could be easily changed to accomodate the change in concentration of the contaminants during the clean up process.

Innovative Processes

There are a number of innovative, generally unproven, processes that potentially can be applied to in situ biorestoration. These processes include land treatment, techniques that decrease the surface tension to enhance the mobility and improve the biodegradability of the contaminants, application of enzymes, and treatment beds.

Land treatment--Land treatment is a process in which the indigenous microflora in surface soils degrade the organic material contained in the soil. Loehr and Malina (1986) suggested that land treatment is useful for disposal of organic wastes from municipal sludge, petroleum, wood preserving, leather tanning, coal gasification/ liquefaction, food processing, and pulp and paper production. Land treatment involves the addition of the organic waste to the soil, mixing to aerate and incorporate the organics into the soil and, if needed, adding fertilizer to stimulate microbial activity. The process must be carefully managed to prevent overloading the assimilative capacity of the soil and to prevent migration of the inorganic nutrients, organics, and heavy metals (Ross and Phung, 1983). Major factors that control biodegradation in land treatment are listed in Table 2-7. Land treatment

45

Table 2-6.   Types of Aquifers Where In Situ Biostimulation Has Been Utilized

Aquifer Description	Flow Characteristics	Reference
high permeability dolomite	pumping rate of 265 to 378 L/min	Raymond et al., 1976 Raymond et al., 1975 Jamison et al., 1975 Jamison et al., 1976
medium to coarse sand	pumping rate of 65 to 151 L/min	Raymond et al., 1986
alluvial fan deposit of sand, gravel, and cobbles with some clay and silt	flow of 2.4 m/day	Minugh et al., 1983
poorly sorted mixture of boulders, pebbles, cobbles, sand, silt and clay	hydraulic conductivity of 9.4×10^{-5} to 1.7×10^{-3} cm/sec	Jhaveri and Mazzacca, 1983 Jhaveri and Mazzacca, 1985
perched water table in unstratified, unsorted layer of clay, silts, sands, gravels, and cobbles above a clay layer	pumping rate of 38 to to 57 L/min	Quince et al., 1985 Flathman et al., 1985
tank vault filled with pea gravel surrounded by sand and sandy clay strata	flow rate in excess 100 m/yr pumping rate of 151 L/min	Westray et al., 1985 Brown et al., 1985b Brenoel and Brown, 1985
glacial outwash composed of silt, sand, and gravel	hydraulic conductivity of 8.8×10^{-4} to 1.5×10^{-3} cm/sec	Brown and Norris, 1986
coarse sands and gravel	hydraulic conductivity of 2.1 cm/sec	Nagel et al., 1982
shale and siltstone	pumping rate of 68 L/min	Brown et al., 1985b Yaniga et al., 1982 Yaniga et al., 1985b
coarse sand with greater than 5% gravel	gradient of 0.015 to 0.02 m/m; flow of 0.61 to 0.91 m/yr	Yaniga and Mulry, 1984

(Continued)

Table 2-6. (Continued)

Aquifer Description	Flow Characteristics	Reference
glacial till composed of sand, gravel, and boulders in a silty clay matrix connected to a fractured sandstone		Yaniga et al., 1985b
shallow basin containing sand and pea gravel	flow of 27 to 38 L/min	Flathman and Githens, 1985

Table 2-7. Factors That Control Biodegradation in Land Treatment (Huddleston et al., 1986)

1. Chemical structure of the waste

2. Presence of appropriate numbers of microorganisms capable of degrading the wastes

3. Concentration of the wastes

4. Supply of oxygen

5. Optimal water content of between 25 and 85% of the water holding capacity

6. Optimal temperatures between 20 and 30°C

7. Optimal pH levels between 6 and 8

8. Availability of inorganic nutrients, principally nitrogen and phosphorus

may be advantageous in comparison to other remedial techniques because it requires minimal operation and maintenance and is a proven technology for some wastes (Reible and Wetzel, 1983). However, the process may result in incomplete destruction of the organic wastes, the soil may be difficult to aerate effectively, the wastes must be contained within the treatment zone, air pollution may result, and large areas of land are required. Land treatment is usually limited to the upper 1.5 m of soil (Ryan et al., 1986) which restricts its use in aquifer remediation. However, land treatment may be used to treat excavated soil or wastes that are concentrated at the water table of shallow aquifers. Law Engineering Testing Company (1982) recommended that land treatment of ground water contaminated with gasoline be considered when a suitable site is available. In comparison to other treatment technologies, land treatment was rated highly on the basis of effectiveness, capital costs, reliability, and operability (Kebe and Brockman, 1984).

Land treatment was used to treat a spill of 1.9 million liters of kerosene (Dibble and Bartha, 1979). About 200 m^3 of soil was excavated and the contaminated ground water was withdrawn and treated. The contaminated soil was treated by adding lime and fertilizer (nitrogen, phosphorus, and potassium in the ratio of 10:1:0.85) and frequently tilling the soil to a depth of 46 cm. The fastest rate of kerosene degradation occurred during the warmer months of July and August. The concentration of kerosene was reduced from 0.87 percent to innocuous levels in the upper 30 cm of soil during a 21 month period. However, kerosene persisted at a depth of 30 to 45 cm, perhaps a result of reduced aeration. Within the first seven months, most of the n-alkanes and unresolved hydrocarbons were degraded. A test for phytotoxicity after land treatment indicated that the phytotoxicity of the kerosene had been reduced but not completely eliminated; crop yields were 20 percent below those in a control area 23 months after the spill.

Techniques that reduce the interfacial tension--Insoluble organic compounds that are sorbed to soils can be mobilized and made more available for microbial attack by decreasing the interfacial tension between the compounds and water. The interfacial tension can be decreased with dispersants, surfactants, extractants, and emulsifiers. Dispersants have been used in remediation programs to control marine oil spills with some success (Colwell and Walker, 1977). Addition of disperants can increase the rate of reaction, but may not increase the extent of hydrocarbon degradation. However, not all dispersants enhance degradation of hydrocarbons and some may be toxic to microorganisms. Mulkins-Phillips and Stewart (1974a) reported that only one of four dispersants stimulated biodegradation of crude oil by marine bacteria; however, all four dispersants caused shifts in the microbial population.

The addition of surfactants to mobilize organics sorbed to soils has been tested in laboratory studies. A combination of nonionic and ionic surfactants was most effective in removing gasoline from sand columns by simple displacement and by draining the capillary zone of the gasoline (Texas Research Institute, 1979). Some of the surfactants identified in this study were biodegradable whereas others exhibited varying degrees of toxicity. Ellis et al. (1984) demonstrated that surfactants could remove up to 95 percent of the crude oil and polychlorinated biphenyls trapped in sand columns whereas aqueous washes failed to remove appreciable quantities of these contaminants. Surfactants may be used in combination with biorestoration to remediate aquifer contamination problems. A surfactant wash can mobilize the residual hydrocarbon in the unsaturated zone and render trapped hydrocarbon in the saturated zones more available for biodegradation (Wilson and Ward, 1986). A surfactant which is biodegradable and non-toxic is required. The application of surfactants to subsurface contaminants may present additional environmental problems by spreading contaminants to sections of the aquifer previously uncontaminated.

Emulsifers can be used to increase the surface area and render the oil more degradable (Atlas, 1977). Emulsifiers can be either chemical additives or biological agents. Robichaux and Myrick (1972) reported that one chemical emulsifier increased the microbial decomposition of oil eighteen-fold; however, other emulsifiers were less successful and many may have been toxic. Broderick and Cooney (1981) reported that emulsifiers are produced by a variety of organisms in freshwater environments, especially those associated with sediments. Laboratory studies conducted by Vanlooke et al. (1978), showed that 10-20 percent of the oil adsorbed to soil was removed after the addition of a nutrient solution containing ammonium nitrate and peptone; microbial metabolities were thought to be responsible for the enhanced desorption. The ground water microflora in an aquifer contaminated

with aviation fuel was reported to emulsify hydrocarbon when supplied with dissolved oxygen, nitrogen and phosphorus (Ehrlich et al., 1985). Micelles and microemulsions of the hydrocarbon are likely to be formed by bioemulsifiers which may facilitate transport of the hydrocarbon into the cell (Wilson, 1986). Biosurfactant-producing bacteria may be used to remediate contaminated aquifers but their use will be controlled by: 1) the physical and chemical characteristics of the contaminant, 2) the geophysical and geochemcial characteristics of the formation such as pore size distribution and permeability, water quality, and oxygen concentration, and 3) competition with indigenous microflora. The hydrocarbon that is mobilized as a result of bioemulsification may be withdrawn from the aquifer and treated by above ground techniques (Wilson et al., 1986). The microbial conversion of the hydrocarbons to more polar compounds such as alcohols, ketones, phenols, or organic acids will also mobilize the contaminants.

Another application of bioemulsifiers is enhanced oil recovery. Clark et al. (1981) found several aerobic microbial species that could be used to bioemulsify oil in situ. Zajic and Akit (1983) found two bacterial strains that produced high concentrations of surfactants; one could remove bitumen from tar sands when grown on hexadecane. A bacterial culture supported on molasses was able to release 19.5 to 48.7 percent and utilize 2 to 51 percent of the oil in a formation within 10 days (Lazar, 1983). Field trials were successful in two of seven reservoirs, increasing yields by 10 to 200 percent.

Extraction techniques such as steam flooding, alcohol flooding, and thermal flooding also may be used to mobilize organic contaminants in the subsurface; however, they have not been demonstrated in the field (Wilson and Conrad, 1984). Horizontal or vertical water sweeps can be used in permeable aquifers to reduce the quantity of hydrocarbons before treatment by other methods such as in situ biorestoration.

Enzymes as an innovative treatment technique--Another innovative in situ process is the addition of enzymes to degrade specific organic compounds. In one investigation, a parathion hydrolase enzyme isolated from a mixed culture of Pseudomonas was added to wet and dry plots of soil amended with the organic phosphorus insecticide diazinon (Paulson et al., 1984). In both wet and dry plots, removal was initially faster in the enzyme-amended soil than in the control; however, diazinon levels in the test and control plots were similar after 408 hours. The effectiveness of an enzyme depends upon its stability in the enviromnment and contact with the substrate. Adequate mixing to insure contact may be difficult to achieve in an aquifer. In addition, enzymes may be better substrates for microbial metabolism than many organic pollutants. The stability of an enzyme in the environment may be adversely affected by changes in pH and solute concentrations.

Treatment Beds--Treatment beds are another innovative process currently under development. The process consists of a trench which intercepts contaminated ground water and either a biological or chemical treatment bed which removes the contaminants. Chemical treatment beds for organic compounds include activated carbon or synthetic resins (Ehrenfeld and Bass, 1984). Biological treatment can be accomplished using processes similar to trickling filters in which microorganisms colonizing a surface are supplied with oxygen and nutrients, if necessary, and degrade the contaminants which enter the treatment bed. Permeable treatment beds may plug or exhibit channeling, which reduces their effectiveness. Similar results could be obtained without the treatment bed by implementing in situ biorestoration in a narrow zone that intercepts and contains the plume.

Potential for Anaerobic Processes

Anaerobic degradation pathways in the subsurface--Anaerobic processes are important in the subsurface environment because oxygen may be depleted in contaminated aquifers as a result of aerobic microbial activity. However,low levels of oxygen will support some microbial activity. Once the dissolved oxygen content in ground water declines as a result of microbial activity, replacement depends on recharge, reaeration from soil gases, and mixture with oxygenated waters surrounding the organic plume (Borden and Bedient, 1986; Borden et al., 1986).

Degradation of a variety of compounds under anaerobic conditions has been demonstrated to occur in aquifers and laboratory experiments using subsurface materials. However, anaerobiosis may retard the degradation of many compounds (Hutchins et al., 1985). The sequence of microbial processes that occur as environmental conditions

49

change from aerobic to anaerobic in the subsurface usually follows the pattern of aerobic respiration, denitrification, manganese and iron reduction, sulfate reduction, and finally methane formation (Bouwer, 1985; Downes, 1985). Net energy production decreases as the redox potential decreases (Downes, 1985). Bouwer and McCarty (1983a;1983b) demonstrated differences in the degradation of organic compounds under different redox potentials; chloroform and 1,1,1-trichloroethylene were degraded by methanogenic, but not denitrifying bacteria. Ehrlich et al. (1982; 1983) reported the degradation of phenolics, but not polynuclear aromatics such as naphthalene, under methanogenic conditions. Recently Kuhn et al. (1985) documented removal of tetrachloroethylene, the xylene isomers, and dichlorobenzene isomers under denitrifying conditions. Wilson and Rees (1985) showed that degradation of benzene, ethylbenzene, toluene, and o-xylene occurred in methanogenic aquifer material from a landfill, although the process was slow compared to aerobic pathways. The concentration of toluene had been reduced by 87 percent after six weeks, however, more than 20 percent of the benzene, ethylbenzene, and o-xylene added to the microcosms persisted beyond 40 weeks. In the same study, trichloroethylene and styrene degraded under anaerobic conditions, whereas chlorobenzene persisted. Suflita and Gibson (1985) reported that 13 of 19 halogenated isomers of benzoate, phenol, and phenoxyacetate persisted at concentrations greater than 90 percent of that initially added to subsurface materials collected from a sulfate-reducing zone; however, only 3,4-dichlorobenzene remained at concentrations greater than 5 percent of that originally added to methanogenic samples collected downgradient of the sulfate reducing zone. Maximal numbers of sulfate-reducing and methanogenic bacteria are found at redox potentials of -100 to -150 and -250 to -350 mV, respectively (Van Engers, 1978). Halogenated aliphatics such as trichloroethylene, tetrachloroethylene, carbon tetrachloride, and 1,1,1-trichloroethane can be mineralized or dehalogenated under reducing conditions (Parsons et al., 1985) to potentially more toxic compounds such as vinyl chloride (Vogel and McCarty, 1985; Wood et al., 1985).

Anaerobic processes in in situ biostimulation--Anaerobic processes may be of potential use in in situ biorestoration processes. The redox potential would be selectively adjusted to favor the degradation of a particular contaminant. In addition to adjusting the redox potential, the pH of the ground water could be adjusted to the neutral or alkaline conditions required for sulfate reduction, methanogenesis, and usually denitrification. Anaerobic degradation of organic compounds would probably require less inorganic nutrient supplementation because less energy and therefore biomass is produced (Rittman and Kobayshi, 1982). Batterman (1983) added nitrate to ground water contaminated with hydrocarbons in an attempt to promote denitrification. The contaminated aquifer consisted of an 8 to 10 meter thick layer of sand which contained some silt and clay beds and a ground water flow of 4 m/day. The water was withdrawn from a deeper uncontaminated aquifer, aerated, passed through a sand filter, and amended with nitrate at 300 mg/L before being recharged to the shallow aquifer. Phosphate was not added because it was not limiting. The authors suggested that anaerobic degradation accounted for the removal of 7.5 tons of hydrocarbon within a period of 120 days. Removal of 1 mg of the hydrocarbon required 3.3 mg of nitrate (Batterman and Werner, 1984). The concentration of aliphatics declined slowly from 1.5 to about 0.7 mg/L whereas the total aromatics declined from 5.5 mg/L down to about 1.5 mg/L in approximately one year. The rate of decline in the concentration of xylene was much slower than that of benzene and toluene. Water was injected during the test which resulted in a rise in the level of the hydrocarbons as well as the water table into the unsaturated zone. There was an overall 40 percent reduction in the concentration of hydrocarbon as a result of the treatment process. Insufficient information was provided to determine if anaerobic degradation was responsible for the removal of the contaminants or if the removal was due to the oxygen introduced when the injection water was aerated before it was recharged into the shallow aquifer.

Degradation of low concentrations of organic compounds under methanogenic conditions, with acetate added at higher concentrations as a primary substrate, has been demonstrated (Bouwer, 1985). McCarty (1985) proposed a scheme to treat contaminated ground water anaerobically using the primary substrate concept. The system consists of an above ground reactor to which substrate and nutrients are added, a well casing bioreactor which operates anaerobically like a trickling filter, and the aquifer. The above ground reactor is used to develop an acclimated population. The effluent from the above ground reactor is injected into the well casing bioreactor to introduce acclimated microbes into the aquifer or enhance adaptation of the indigenous population to the contaminants. Once the acclimated population has devloped, use of the above ground reactor can be discontinued.

A method that utilizes sequential aerobic and anaerobic conditions to degrade hazardous wastes has been studied in soils and may be applicable to subsurface cleanup. An insecticide, methyoxychlor, was slightly degraded in soil under either aerobic or anaerobic conditions after three months of incubation. When the samples were converted from an anaerobic to an aerobic status, mineralization of the methoxychlor increased 10 to 70 times of that observed in soils maintained aerobically throughout the incubation period (Fogel et al., 1982). The enhancement in methoxychlor degradation in soils exposed to anaerobic and then aerobic conditions may be a result of dechlorination of the insecticide under anaerobic conditions and degradation of the dechlorinated products under aerobic conditions. This anaerobic-aerobic treatment scheme may be useful in biorestoration of aquifers contaminated with halogenated compounds. The aquifer could be managed like a sequencing batch reactor in which an acclimated population is exposed to deoxygenated water, then to aerobic conditions and then the treated water is withdrawn. The hydraulically managed system is then allowed to sit idle until the next cycle is initiated.

Rates of degradation under anaerobic conditions are typically slower than those under aerobic conditions; in addition, organic compounds may not be mineralized under anaerobic conditions even after long periods of incubation (Wilson and Rees, 1986). However, anaerobic treatment may be required to degrade pollutants that are recalcitrant under aerobic conditions; also, anaerobic treatment may require less management. The application of anaerobic conditions to biorestoration is still in the development stage and more research is required to demonstrate its usefulness in the field.

3. Addition of Specialized Microbial Populations to the Subsurface

In addition to stimulating the indigenous microbial population to degrade organic compounds, another innovative but not yet demonstrated technique is to add microorganisms with specific metabolic capabilities (Lee and Ward, 1985b). Specialized organisms may be inoculated into the subsurface environment or the environment may be altered to favor growth of a population with specific metabolic capacities. Populations that are specialized in degrading target compounds are selected by enrichment culturing or genetic manipulation. Enrichment culturing involves exposure of microorganisms to increasing concentrations of a contaminant or mixture of contaminants. The type of microorganisms that is selected or in essence, acclimates to the contaminant, depends on the source of the inoculum, the conditions used for the enrichment, and the substrate (Atlas, 1977). Acclimation can result from an increase in the number of organisms that can degrade the contaminant, new metabolic capabilities that result from genetic changes, or an increase in the quantity of the enzymes necessary for the transformation (Spain et al., 1980). The genetic changes include overproduction of enzymes, inactivation or alteration of regulatory gene control, or production of enzymes with altered specificities (Ghosal et al., 1985).

Genetic manipulation of microorganisms to produce specialized populations that can degrade target contaminants is a relatively recent development. According to Kilbane (1986), genetic engineering may accelerate and focus the process of evolution. Genetic manipulation can be accomplished by two different methods. In the first method, the organisms are exposed to a mutagen such as ultraviolet light, nitrous oxide, or 8-azaquinonone and then a population with specialized degradative capabilities is isolated by enrichment culturing (Zitrides, 1978; Kopecky, 1982); however, this may produce weakened strains because the process is non-specific and affects the entire genome (Zitrides, 1978). In the second method, recombinant DNA technology is used to change the genetic structure of the microorganism (Kilbane, 1986). The genetic structure is changed by inserting a DNA fragment, often a plasmid that codes for a specific degradative pathway, into another organism. A plasmid is a piece of DNA that exists independently from the cell's chromosomes (Birge, 1981). The extra-chromosomal DNA can be transformed from one bacterium to another by conjugation, transduction, or transformation. Multiple degradative capabilities can be placed on a single plasmid that will allow the organism to degrade an array of compounds or complete the degradation of a nonbiodegradable molecule. Genetic engineering can be used to stabilize the degradative traits coded by the plasmid, increase the number of plasmids in a cell, amplify enzyme production and activity, invoke multiple degradative traits, or produce a novel degradative pathway (Pierce, 1982). In addition, organisms with different substrate affinities, pH optima, or degradation rates can be fashioned (Johnston and Robinson, 1982a).

Genetic Engineering to Enhance Degradative Activity--

Genetic engineering has been used to enhance the degradation of the recalcitrant pesticide, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). Biodegradation of the pesticide is usually very slow (Kilbane et al., 1982). A mixed culture of microorganisms that uses 2,4,5-T as a sole carbon and energy source was obtained by a technique called plasmid-assisted molecular breeding (Kellog et al., 1981). The technique involves inoculating a chemostat with microorganisms from a variety of hazardous waste sites and organisms that carry an array of plasmids that code for degradation of specific xenobiotics. A pure culture that could use 2,4,5-T as a sole carbon and energy source was isolated from the mixed population and tentatively identified as Pseudomonas cepacia (Kilbane et al., 1983). In addition, the culture, designated P. cepacia AC1100, was reported to oxidize many chlorophenols. Degradation of both 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-T was expressed in another strain of P. cepacia after conjugal transfer of two plasmid from an Alcaligenes entrophs sp. that degraded some chlorinated phenoxy herbicides (Ghosal et al., 1985). An inoculum of 2 x 10⁷ cells/g of P. cepacia AC1100 degraded 95 percent of the 1,000 mg/L 2,4,5-T added to soil at 25 percent moisture and incubated at 30°C (Chatterjee et al., 1982). Less 2,4,5-T was removed with a smaller inoculum size and different temperatures and moisture contents. In addition, the 2,4,5-T degrading bacteria did not survive in soil without 2,4,5-T or when the concentration of the compound had been depleted (Kilbane et al., 1983). Field trials to determine the effectiveness of the 2,4,5-T-degrading bacteria have not been conducted.

Colaruotolo et al. (1985a) received a patent for "microbial degradation of obnoxious organic wastes into innocuous materials." The process involves isolation of microbial cultures from samples of soil and leachate from a hazardous waste site by enrichment culturing and then application of the purified strains in the field to remove the contaminants. Microorganisms capable of degrading selected isomers of chlorotoluene, dichlorotoluene, and dichlorobenzoate were isolated. Conjugation and transformation experiments were conducted to transfer the plasmid DNA, which conferred the ability to degrade some chloroaromatics, from the original isolates to another organism. The patent claimed that the organisms could be used to decontaminate soil, remove contaminants in the air, mineralize toxic organics in the leachate from a chemical landfill and thereby reduce the concentrations of noxious chemicals.

Issues in Genetic Engineering of Microbes--

Organisms that can not easily exchange their genetic information with other organisms and are restricted to growth under defined environmental conditions are preferred candidates for genetic manipulation (Pierce, 1982). Issues concerning the use of genetically engineered organisms in the environment include: 1) adverse effects on human health, 2) how to effectively monitor their dispersal, 3) survival of the engineered organism in the environment, 4) regulation of activity in nontarget areas; and 5) determination of set risk levels acceptable to the public (Joyce, 1983). Many scientists argue that the engineered organism is not radically different from that which is genetically unaltered. The release of genetically engineered organisms into the environment is of great concern and some time may elapse before these organisms are used (Fox, 1985). The survivability of genetically altered organisms in the environment is also of concern. Surrogates of genetically engineered organisms which carried antibiotic resistance were added to samples of sewage, lake water, and soil and survived at rates that varied with the strain and environment tested (Liang et al., 1982). Some of the antibotic-resistant strains reached steady-state concentrations in lake water and sewage; however, all strains declined in the soil after a period of one month. Pseudomonas strains that degrade 2,4-dichlorophenol and p-nitrophenol were isolated from soil by enrichment culturing techniques. The ability of the isolates to degrade the phenol derivations was variable when inoculated into lake water, sewage, and soil (Goldstein et al., 1985).

Inoculation of a specialized microbial population into the environment may not produce the desired results for many reasons (Table 2-8). The concentration of the target compound required to support activity of a specific degrader may be limiting. Toxic or antimicrobial substances such as antibiotics may be found in many environments. High density inocula may be grazed by predators and the degradative capacity severely decreased if the growth rate of the introduced organisms is slow. In addition, adequate mixing to ensure contact of the organism with the pollutant will be difficult to achieve in the subsurface.

Table 2-8. Reasons Why Introduced Organisms Fail to Function in the Environment (Goldstein et al., 1985)

1. The concentration of the compound is too low

2. The environment contains some substance or organisms that inhibit growth or activity, including predators

3. The inoculated organism uses some other organic other than the one it was selected to metabolize

4. The organic is not accessible to the organism

Most hazardous waste sites involve contamination of the environment with more than one compound. Therefore a mixture of organisms may be necessary to degrade all of the compounds in the waste (Atlas, 1977). Populations that have adapted to degrade many organic contaminants may be isolated from biological treatment processes such as sewage treatment, which receive pollutants. The efficacy of an inoculated population of specific degraders will depend on environmental constraints such as temperature, pH, and the concentrations of substrate, nutrients, and oxygen (Atlas, 1977; Zajic and Daugulis, 1975). Successful results from inoculation of foreign organisms are more likely in simple environments because the environment can be controlled more easily. An example of inoculation into a simple environment would be the introduction of bacteria into a biological reactor, oil tanker ballast tanks, or fermentator; these also provide the benefit of containing the microorganisms. To avoid problems encountered with inoculation of foreign organisms into the environment, samples from the contaminated environment can be collected, microorganisms that can degrade the pollutants can be cultured by enrichment techniques or genetically engineered, and finally the specialized population can be reintroduced into the environment from which they came (Omenn, 1986). In addition, genetic manipulation of oligotrophic bacteria with high affinity enzyme systems may be advantageous because these enzyme systems will allow the organism to attack low concentrations of organic pollutants (Johnston and Robinson, 1982b).

Seeding Aqueous Environments with Microorganisms--

Inoculants of specialized microorganisms have been used in treatment of contaminated water. Atlas and Bartha (1973) tested several commercial bacterial preparations and found that the inocula were ineffective in treating oil spills in the marine environment. However, the addition of fertilizer and a bacterial seed isolated from an estuarine environment increased petroleum degradation in a saline but not in a freshwater pond (Atlas and Busdosh, 1975). After six weeks, 50 percent of the oil remained in the saline pond. The lack of activity in the freshwater pond suggests that the inoculum should be cultured from an environment similar to that being treated. Colwell and Walker (1977) suggested that seeding would be unsuccessful in environments such as the ocean; however, contained spills and lagoons may be amenable to such treatment. Gutnick and Rosenberg (1977) stated that "there is no evidence to support the claim that "seeding" oil slicks with microorganisms reduces oil pollution by stimulating petroleum biodegradation."

Seeding Soil Environments with Microorganisms--

The efficacy of inoculating soil with acclimated bacteria to remove selected contaminants was tested in a series of experiments (Wetzel et al., 1981) using experimental chambers set up in greenhouses. The contaminants, aniline and formaldehyde, were added to three types of soils (clay, sandy loam, and organic-rich) and plants were seeded in the chambers. Removal of the contaminants by a mixed microbial population from primary sewage effluent and an acclimated population was investigated. Formaldehyde was not removed in organic soils amended with sewage and acclimated bacteria; however, this treatment was successful in the upper and middle zones of the sand and clay soils. Aniline was removed in the organic and sandy soils after a second application of sewage microorganisms, nutrients, and yeast extract. Chemical oxidation of the organics using hydrogen peroxide was

effective in reducing aniline concentrations. None of the treatments were successful in removing aniline from the clay soil. The removal of chlordane and 2,4-dinitrophenol by mutant adapted microbial cultures was also investigated. The inoculum was successful in degrading 2,4-dinitrophenol from the upper layer of the clay soil only. The authors suggested that the sewage inoculum was a low cost, effective method for removal of aniline and formaldehyde in most soil types; however, addition of the adapted population was not successful in these tests.

Inoculation of soils to remove chlorinated organics and pesticides has been attempted. Daughton and Hsieh (1977) reported that inoculation of sterilized soils with a parathion-acclimated culture reduced the concentration of the insecticide by 85 percent; however, the efficiency of the inoculum in non-sterile soil was greatly reduced. Focht and Brunner (1985) used an Acinetobacter strain as an inoculum to degrade biphenyl and polychlorinated biphenyls in soils. The inoculum increased the initial and maximum mineralization rates and the disappearance of the more heavily chlorinated biphenyls, but the overall extent of mineralization of polychlorinated biphenyls was not greater than that in inoculated soil to which biphenyl had been added. The process was thought to be a cometabolic-commensal metabolism of the PCBs.

Remediation of soil contaminated with hydrocarbons by inoculating with hydrocarbon degrading organisms has been met with varying success. Schwendinger (1968) demonstrated that inoculation of a hydrocarbon- degrading strain of Cellumonas in soil contaminated with petroleum increased the rate of reclamation in comparison to soils amended with only nutrients. Jobson et al. (1974) reported that the application of 10^6 cells of oil-degrading bacteria per cubic cm of soil slightly increased the degradation of the C_{20}- to C_{25}- group of n-alkanes in comparison to soils amended with fertilizer only. However, Lehtomaki and Niemela (1975) reported that brewer's yeast added to soils served primarily as a fertilizer rather than as an inoculum to actively degrade the oil. Seeding boreal soil with an oil-degrading inoculum increased microbial activity (Hunt et al., 1973). In laboratory studies, the addition of 300 ppm nitrogen and 100 ppm phosphorus, inoculation, and adjusting the pH to 7, increased microbial activity by at least a factor of four in comparison to unamended samples after 40 days of incubation. An increase in plant growth in an oil contaminated area in response to fertilizer addition was shown in field studies; however, the increased growth could have resulted from the addition of fertilizer or enhanced removal of the petroleum. In contrast, Westlake et al. (1978) reported no beneficial effects from the addition of oil-degrading bacteria to boreal soils. The lack of enhancement may be a result of inadequate application of the inoculum. The type of organisms isolated from enrichment culturing depends on conditions used during the isolation procedure. For example, enrichments made at 4 and 20°C contained different organisms, and cultures enriched on a low quality crude were better adapted to utilize a lower quality crude than cultures enriched on a high quality crude (Jobson et al., 1972). These data suggest that enrichments for specialized populations should be conducted using the environmental conditions and contaminants that are unique to the site under investigation.

An inoculum of pentachlorophenol-degrading organisms has been used to decontaminate soil, river water, ground water and other freshwaters (Martinson et al., 1984). A Flavobacterium sp. that could mineralize pentachlorophenol (PCP) was isolated from a man-made channel which was exposed to the compound for several weeks (Crawford and Mohn, 1985). In addition to mineralizing PCP, the microorganism could attack a number of other chlorinated phenols but not all isomers (Steiert and Crawford, 1985). The Flavobacterium sp. at a cell density of 10^6 cells/ml removed over 90 percent of the PCP added to river water, ground water and other fresh waters, usually within 48 hours (Martinson et al., 1984). The organisms ability to degrade PCP was best between 15 and 35°C, and at pH values between 7.5 and 9.0. Inoculum densities as low as 10^4 cells/ml resulted in efficient removal of PCP. The time required to remove the PCP increased with increasing concentrations of PCP. When added to uncontaminated soil, the PCP was rapidly mineralized (Crawford and Mohn, 1985). The highest extent of mineralization occurred in soils with moisture contents between 15 to 20 pecent.

Mineralization of PCP was observed at inoculum densities as low as 3.1×10^3 cells/g; however, a slightly higher extent of mineralization was observed at a cell density of 3.1×10^6 cells/g (Crawford and Mohn, 1985). Mineralization of PCP in one uninoculated soil began after seven days of incubation and mineralization proceeded to the same point as the sample inoculated with 10^7 cells/g. Concentrations of PCP in soil contaminated from a wood treating landfill were reduced from 298 to 58 ppm after four applications of the inoculum in a period of 100 days. In another contaminated soil, PCP levels were reduced from 321 to 41 ppm after one application of seed,

54

but similar levels of removal were observed in the uninoculated control. The seed could not remove PCP from a third soil in which the concentration of PCP had been diluted 10 fold to 553 ppm and the pH adjusted to neutrality. Addition of 10^6 cells/g soil of a culture of PCP-degrading Arthrobacter sp. reduced the half-life of PCP from two weeks to 15 hours (Finn, 1982). Edgehill and Finn (1983) reported that the rate of PCP disappearance was proportional to inoculum size that ranged from 10^4 to 10^6 cells/g soil. Up to 85 percent of the PCP was removed within 12 days in soil in which the seed had been thoroughly mixed; however, only 50 percent was removed in the unmixed soil. Brown et al. (1986) suggested that fixed film reactors with a PCP-adapted population may be used to treat waters contaminated with PCP at concentrations below the threshold of toxicity. A consortium that was attached to rocks from an artificial stream amended with PCP was generally able to degrade PCP as fast as the Flavobacterium sp. described by Crawford and Mohn (1985). A treatment system using two fixed film reactors in series was then proposed; the first reactor would reduce high concentrations of PCP and the second reactor would contain organisms that could remove PCP to low levels. The consortium was able to remove PCP to less than 1 mg/L when the initial concentrations were less than 1 mg/L.

Seeding the Subsurface with Microorganisms--

Inoculation of bacteria into the subsurface for biorestoration has been met with some success, but the contribution of the introduced bacteria to the overall cleanup can not be readily determined. In most cases, the role of the introduced bacteria in degradation of the contaminants can not be determined because appropriate control plots were not incorporated into the experimental design and the results were not quantitatively measured throughout the course of the project. The biggest concern of inoculation into the subsurface is ensuring contact between the specialized cells and the target contaminants. The cells may be filtered out of the perfusing solution or sorbed onto soil before reaching the contaminants (Bouwer, 1984). In addition, normal die-off may control the movement and spread of bacteria in well-sorted sand, gravels, fractured rock, and karstic limestone.

Microbial movement through the subsurface depends on the characteristics of the soil and microorganisms. Only 1 percent of an inoculum of a Pseudomonas strain passed through a 2-inch sandstone core after washing with 123 pore volumes (Jenneman et al., 1984). Penetration of bacteria into sandstone cores with hydraulic conductivities greater than 100 millidarcies was rapid; however, penetration in cores with hydraulic conductivities below 100 millidarcies was slow (Jennemen et al., 1985). Motile bacteria moved three to eight times faster than nonmotile bacteria. Hagedorn (1984) summarized the results of selected studies on the maximum distance that microorganisms moved in various soils: 19.8 m in 27 weeks in a fine sand; 10.7 m in a sand and sandy clay in eight weeks; 24.4 m in a fine and coarse sand (time of travel not reported); 30.5 m in a sand and pea gravel aquifer in 35 hours; 0.6 to 4 m in a fine sandy loam (time of travel not reported); 457.2 m in a coarse gravel aquifer in 15 days; 28.7 m in 24 to 30 hours in a crystalline bedrock. Bacteria have moved as far as 920 meters in the subsurface at rates up to 350 m/day (Gerba, 1984). Microbial movement through soil macropores is an important mechanism of transport in all subsurface soils except sandy soils and those that are disturbed (Smith et al., 1983).

Transport of microorganisms in the subsurface can occur. However, in situ biorestoration programs using inoculation techniques will be affected by adverse conditions that decrease the survivability of microorganisms in the environment. Several factors must be considered before an in situ biorestoration program utilizing acclimated bacteria is implemented. The source, quantity, nature and biodegradability of the contaminants, and the environmental conditions of the site must be determined (McDowell et al., 1980). In addition, laboratory tests to determine the kinetics of degradation, the potential for inhibition under various conditions, requirements for oxygen and nutrients, and the effects of temperature should be conducted. The formation must be permeable enough to perfuse nutrients and the inoculum through the zone of contamination.

Aquifer Remediation Using Inoculation Techniques--

Inoculation of microorganisms into the subsurface has been used in aquifer remediation in conjunction with wastewater treatment processes. These cases are summarized in Table 2-9. A representative system is shown in Figure 2-3. In one case study, 7,000 gallons of acrylonitrile was spilled in a metropolitan area from a leaking rail car (Walton and Dobbs, 1980). The receiving aquifer contained significant amounts of silt and clay and hence

was rather impermeable. Initial treatment involved withdrawal and treatment of the ground water by air stripping. After the concentration of acrylonitrile had declined to nontoxic levels, mutant bacteria were seeded into the soil. The concentration of acrylonitrile declined from 1,000 ppm to nondetectable levels (limit of detection 200 ppb) within one month; however, the role of the bacterial seed in acrylonitrile degradation could not be determined.

Table 2-9. Summary of Aquifer Remediation Case Histories Utilizing Introduced Organisms

Compound	Treatment Description	Reference
acrylonitrile	mutant bacteria added after concentrations had been reduced by air-stripping	Walton and Dobbs, 1980
phenol and chlorophenol	initial treatment by adsorption onto GAC followed by innoculation with mutant bacteria	Walton and Dobbs, 1980
ethylene glycol and propyl acetate	treatment above ground and later with specialized bacteria	Qunice and Gardner 1982a and b
dichlorobenzene, dichloromethane, and trichloroethane	initial treatment with air stripping and then innoculation with a hydro-carbon-degrading bacteria	Quince and Gardner, 1982a and b
unidentified organic compounds	hydrocarbon-degrading bacteria added after levels reduced by GAC and air stripping	Ohneck and Gardner, 1982
formaldehyde	commercial degrader added to above ground treatment system formed from rail ballast	Sikes et al., 1984

Quince and Gardner (1982a; 1982b) documented the cleanup of 100,000 gallons of various organic compounds, including ethylene glycol and propyl acetate, over a 250,000 square foot area. The soil consisted of a thick silty clay that extended to a depth of more than 50 feet; migration of the organics into the main aquifer was prevented by the structure of the formation. Containment and recovery of the organics were limited to the perched water table located in the upper clay layer. The contaminated ground water was withdrawn and treated by clarification, aeration, and granular activated carbon. A biostimulation program with specialized bacteria, nutrients, and air was initiated after the levels of the contaminants had decreased from 2,000-10,000 ppm to less than 200 ppm. During treatment, the concentration of ethylene glycol was reduced from 1,200 to less than 50 mg/L, propyl acetate was reduced from 500 mg/L to less than 50 mg/L, and the total concentration of spilled compounds declined from 36,000 to less than 100 mg/L. The resulting concentrations of contaminants were acceptable to the regulatory agencies.
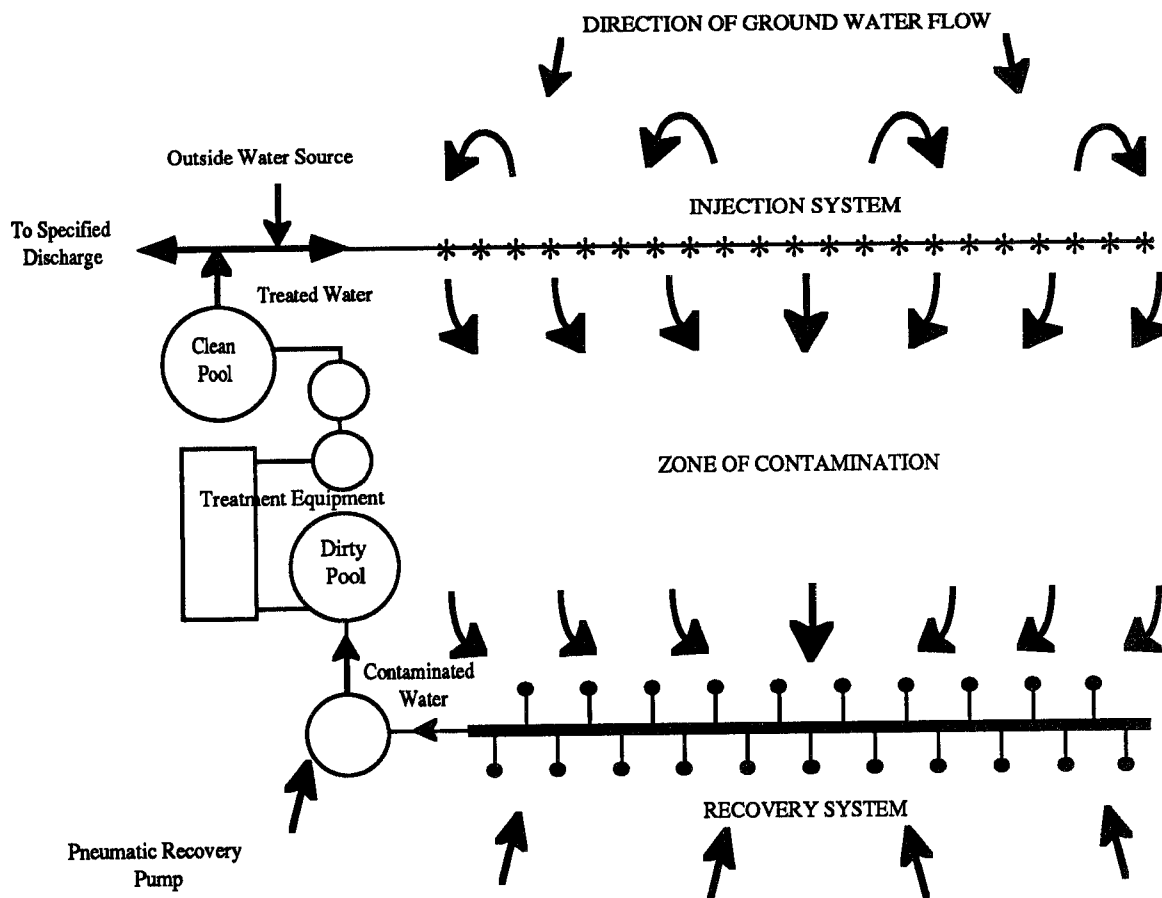
56

Figure 2-3. Combination of above ground treatment with in situ biorestoration.

Quince and Gardner (1982a; 1982b) documented the cleanup of a number of organic chemicals including dichlorobenzene, methylene chloride, and trichloroethane that contaminated the subsurface as a result of a spill from vacuum system, soil flushing, air stripping, and then inoculation of commercial hydrocarbon-degrading bacteria into an above ground reactor followed by recharge of the effluent into the subsurface. A commercial decreased the concentrations of the organic contaminants after 36 hours of exposure. The operation was terminated after a 95 percent reduction in the organic levels was achieved. The injected hydrocarbon degraders were expected to complete the biodegradation in situ; however, the role of the added bacteria was not demonstrated.

An accidental spill of 130,000 gallons of organic chemicals entered a 15 foot thick shallow unconfined aquifer and resulted in total contaminant levels as high as 10,000 ppm (Ohneck and Gardner, 1982). A drinking water aquifer was separated from the contaminated zone by 50 to 60 feet of silty clay. The contaminated ground water was withdrawn and treated by clarification, granular activated carbon adsorption, and air stripping. A program to enhance in situ biological degradation was initiated after the concentration of the organics had declined from as high as 10,000 ppm to 1,000 ppm. The results of laboratory tests indicated that the indigenous bacteria could degrade the contaminants when supplied with nutrients. Application of a commercial bacterial inoculum did not increase the biodegradation rates of the organics; in fact, one compound (unidentified) was degraded slower by the commercial hydrocarbon-degrading inoculum than the indigenous population. Effluent from the treatment system was amended with hydrocarbon degrading bacteria, air, and nutrients, and injected into the vadose zone. As a result, the concentrations of the contaminants in one soil core were reduced from 800 to 150 mg/L in two months. In another area, the concentration of the chemicals in composited soil samples declined from 24,000 to 2,000 mg/L. The concentrations of the organics in the ground water were reduced to less than 1 ppm, which met regulatory approval.

Incorporation of biological treatment into the restoration program decreased the cost of operation and maintenance. The role of the commercial inoculum in the removal of the contaminants could not be determined; in addition, laboratory studies indicated that the inoculum did not enhance biodegradation.

A spill of 20,000 gallons of a 50 percent solution of formaldehyde from a railroad tank car contaminated the soil and railroad bed in Ukiah, California (Sikes et al., 1984). Contaminated surface and ground waters were removed by a vacuum truck and 250 cubic yards of soil were excavated. Approximately 13 million gallons of water was collected. The water was initially treated with hydrogen peroxide to reduce the concentration of formaldehyde from 30,000-50,000 to 500-1,000 ppm by oxidation. See Section II.D. for more details of the use of hydrogen peroxide in this case study. The feasibility of in situ biological degradation of the remaining formaldehyde using a commercial bacterial inoculum was then investigated. A commercial inoculum that contained specially cultured microorganisms was chosen for the project. The biological treatment system consisted of a portable aeration tank, a spray system, and a trickling filter. The ground water was heated to increase the destruction rate and the pH was adjusted as necessary with sulfuric acid or soda ash; nitrogen and phosphorus were added as needed. The inoculum was rehydrated with chlorine-free water and added to the system at a rate of 3 lbs per day. The concentration of formaldehyde in the treatment tank fell from greater than 700 to about 10 mg/L after 24 days. The oxygen uptake rate in the sump ranged from 12 to 82 mg/L hr^{-1} and from 29-51 mg/L hr^{-1} in the ballast gravel. The treatment program was temporarily suspended for a day and the system was flushed. During this period, the concentration of formaldehyde increased greatly; however, a rapid reduction in formaldehyde levels followed. The authors suggest that the removal of the formaldehyde was a result of biological activity, however, they concede that proving the role of microorganisms in formaldehyde degradation would be difficult. In addition, the role of indigeneous and inoculated bacteria in formaldehyde degradation could not be separated.

4. Enrichment of Specific Populations

A strategy often used in industrial microbiology is to search through nature for an organism with specialized metabolic capabilities and then culture that organism in a fermentor to protect it from competition. However, this strategy would be difficult to apply in the subsurface environment because the specialized population must be competitive in addition to performing the desired transformation. Enrichment culturing techniques are often used to isolate organisms with specialized metabolic capabilities. The same concept can be used to identify conditions that favor the colonization of that environment by organisms with special traits.

The microbial utilization of pollutants as carbon and energy sources has already been discussed. This section will emphasize the metabolism of pollutants by microorganisms enriched on other primary substrates.

Oxygenated water-table aquifers are often polluted with chlorinated organic solvents such as trichloroethylene (Wilson and McNabb, 1983; Wilson et al., 1981). The ubiquity of these compounds in oxygenated ground water may result from their resistance to microbial attack under aerobic conditions in the subsurface. However, more recent work has indicated that incubation of soils or aquifer materials with methane, propane, or natural gas will enrich for microorganisms that co-oxidize trichloroethylene and a variety of other halogenated organic compounds (Wilson and Wilson, 1985; Fogel et al., 1986; Strand and Shippert, 1986; Hensen et al., 1985; Henry and Grbic-Galic, 1986; Wilson and White, 1986; U. S. EPA, 1984; and Hensen et al., 1986). This technique may be applicable to in situ restoration of aquifers which are contaminated with chlorinated organic solvents.

Using gaseous aliphatic hydrocarbons as the feedstock for a forced co-oxidation is advantageous because they are non-toxic, relatively inexpensive, and widely available in the form of natural gas, liquified petroleum gas, and propane. However, they do not support anaerobic metabolism. In addition, if the gases are supplied inadvertently at concentrations that result in the microbial depletion of the available oxygen, undesirable by-products such as foul-smelling organics, soluble iron, or hydrogen sulfide should not be produced. The disadvantage to enriching for specialized populations using gaseous aliphatic hydrocarbons is the explosion hazard of the hydrocarbons mixed in air at unsafe concentrations. One constraint on in situ restoration programs is that the reagents must be dissolved in the perfusion water to reach the zone of contamination; hydrocarbons and the oxygen required for their metabolism are not very soluble in water.

Wilson and White (1986) developed a general relationship that may be used to predict the extent of removal of a chlorinated organic as a function of the metabolism of a given amount of hydrocarbon feedstock. The relationship is as follows:

$$C/C_o = e^{-kh} \qquad (2-2)$$

where   C = the final concentration of the halogenated organic to
         be co-oxidized,

       C_o = the initial concentration of the halogenated organic,

       h = the amount of hydrocarbon feed-stock to be consumed,

       k = a utilization constant.

At present, there are limited data available to calculate utilization constants and the generality of the relationship has not been widely tested. The equation may prove to be a powerful tool in the engineering design of in situ biorestoration programs. Some utilization constants for trichloroethylene exist (Wilson and White, 1986). As a paper exercise, the extent of removal of trichloroethylene at a number of critical engineering limitations, including the solubility of methane, propane, and oxygen (24, 62, and 40 mg/L respectively) and the oxygen content of well-oxygenated ground water (taken to be 8 mg/L) was estimated. Equation 2-2 was used to estimate the concentration of trichloroethylene that could be brought down to 5 μg/L, the Maximum Contaminant Level proposed under the Safe Drinking Water Act (U. S. EPA, 1984). To preview the economics of in situ biorestoration, costs of the primary hydrocarbon feedstock were estimated at 25 cents/kg and the cost of oxygen supplied as hydrogen peroxide was estimated at 400 cents/kg oxygen supplied.

The predictions of trichloroethylene degradation by populations supported on gaseous aliphatics using Equation 2-2 are illuminating (Table 2-10). At ambient oxygen concentrations, the reduction in the concentration of trichloroethylene supported on either propane or methane is environmentally insignificant. The reductions supported by saturating concentrations of oxygen will probably be useful, but not sufficient to treat most contaminated water in one cycle; the water will have to be circulated and reinjected with oxygen a number of times, or the oxygen will have to be supplied as hydrogen peroxide. Propane is about three times more soluble in water than methane, and considerably greater removals of trichloroethylene are possible using propane as the feedstock. Finally, the cost of trichloroethylene biorestoration in situ can probably be attributed to the cost of supplying the oxygen.

The quantities of methane and propane are calculated from the equation of Wilson and White (1986), assuming utlization constants for trichloroethylene of 0.075 L water treated/mg methane consumed and 0.10 L water treated/mg propane consumed, and assuming utilization constants for cis- and trans-1,2-dichloroethylene of 0.3 L water treated/mg methane consumed.

Vinyl chloride and cis- and trans-1,2-dichloroethylene commonly occur in ground water contaminated with trichloroethylene, and probably result from the reductive dechlorination of trichloroethylene (Barrio-Lage et al., 1986). Utilization constants for these compounds are not available. Wilson and White (1986) estimated from the data of Fogel et al. (1986) that the constants are greater than 0.03 L water treated/mg methane consumed. These higher utilization constants make aquifers contaminated with these compounds much better candidates for in situ biorestoration (Table 2-10). Hydrogen peroxide will probably not be required to achieve adequate treatment. If the contaminated water is pumped to the surface for treatment, the limited solubility of oxygen becomes much less of a problem. The water can be exposed to any desired volume of air in a fixed-film bioreactor (Wilson and White, 1986).

Table 2-11 summarizes the prospects for biorestoration of aquifers contaminated with specific halogenated compounds. These data were compiled by comparing the relative rates of degradation of these compounds in a variety of experimental systems to the rates of transformation of trichloroethylene, and cis- and trans-1,2-

59

dichloroethylene, then assessing the rates in light of the relationships portrayed in Table 2-10. Prospects are rated "good" if hydrogen peroxide will not be required, "fair" if hydrogen peroxide is required, and "poor" if environmentally insignificant removals can not be attained with or without hydrogen peroxide.

Table 2-10. Estimated Quantities of Oxygen and Methane or Propane Requered to Bring the Concentration of Trichloroethylene, cis- or trans-1,2-Dichloroethylene or Vinyl chloride to 5 µg/L

Initial Concentration		Methane Required		Propane Required		Oxygen Required	
TCE µg/L	DCE or VC µg/L	mg/L	cents per 1000 gal.	mg/L	cents per 1000 gal.	mg/L	cents per 1000 gal.
2,500				62	5.9	230	340
1,000				53	5.0	190	290
250				39	3.7	140	210
100				29	2.7	105	159
30		24	2.5			96	146
17				11	1.0	40	
11		10	0.9			40	
7				2.2	0.2	8	
5.8		2.0	0.2			8	
5.0						0.0	
	6,700	24	2.5			96	146
	1,000	18	1.7			71	107
	100	10	0.9			40	
	9	2	0.2			8	
	5.0	0.0				0.0	

The relationship of Wilson and White (1986) does not presuppose an upper limit on the concentration of the chlorinated contaminant; however, an upper limit obviously exists and toxicity effects have frustrated research in this area. Workers at both Stanford University and R. S. Kerr Environmental Research Laboratory have isolated mixed microbial populations from nature that could degrade trichloroethylene, only to lose the ability to degrade the compound when the primary alkane oxidizer was isolated in pure culture. It is tempting to conclude that the trichloroethylene degrader is not an alkane oxidizer. However, other possibilities exist. In certain mixed cultures or microcosms of aquifers, trichloroethylene started to inhibit oxidation of the hydrocarbon feedstock at a concentration of about 1,000 µg/L (S. Fogel personal communication, unpublished data of John Wilson). This is

far below concentrations that produce toxicity in ordinary heterotrophs. Perhaps the effective toxicant was trichloroethylene epoxide, rather than trichloroethylene itself, and the organism that oxidized the primary hydrocarbon feedstock was protected in mixed populations by other organisms. This toxicity threshold must be more carefully defined to aid in identifying contaminated ground water amenable to biorestoration. This work should be done with mixed-cultures or microcosms, using systems that simulate the conditions in the subsurface environment.

No technique to remediate environmental contamination is universally applicable. However, there should be many contamination incidents where biorestoration through a forced co-oxidation is the technology of choice, either alone or in conjunction with physical containment. Successful application of the approach will require an adequate understanding of the philosophy of the biotransformation, and quantitative information on the nutritional ecology of the active organisms.

Table 2-11. Prospects for Treatment of the Common Halogenated Organic Contaminants in Aquifers Through Co-Oxidation Supported on Gaseous Alkanes

Compound	Pump and Treat	Treat in the Aquifer	References
Tetrachloroethylene (PCE)[a]		None	Fogel et al., 1986 Hensen et al.,1985 Hensen et al.,1986
Trichloroethylene (TCE)	Good	Fair	Wilson and Wilson, 1985 Fogel et al., 1986 Hensen et al., 1985 Hensen et al., 1986 Wilson and White, 1986
cis-1,2-Dichloroethylene		Good	Fogel et al., 1986 Hensen et al., 1985 Hensen et al., 1986
trans-1,2-Dichloroethylene		Good	Fogel et al., 1986 Hensen et al., 1985 Hensen et al., 1986
Vinyl chloride direct utilization may be possible		Good	Fogel et al., 1986 Hartman et al., 1985
1,1-Dicholoroethylene		Fair	Fogel et al., 1986
Carbon tetrachloride[a]		None	Hensen et al., 1985 Hensen et al., 1986

(continued)

Table 2-11. (Continued)

Compound	Pump and Treat	Treat in the Aquifer	References
Chloroform		Poor	Strand and Shippert, 1986 Hensen et al., 1985 Hensen et al., 1986
Methylene chloride direct utilization may be possible		Fair	Henson et al., 1986 Flathman et al., 1985
1,1,1-Trichloroethane (TCA)	Poor to Good	Poor	Hensen et al., 1985 Hensen et al., 1986 Wilson and White, 1986
1,1,2-Trichloroethane (TCA)		Poor	Hensen et al., 1985 Hensen et al., 1986
1,1-Dichloroethane (TCA)		Poor	Hensen et al., 1985 Hensen et al., 1986
1,2-Dichloroethane direct utilization may be possible		Poor	Hensen et al., 1985 Hensen et al., 1986 Wilson and McNabb, 1983 Janssen et al., 1985
1,2-Dibromoethane (EDB) direct utilization may be possible		Fair	Hensen et al., 1985 Hensen et al., 1986

ªRemoval of carbon tetrachloride and tetrachloroethylene seen in the soil exposed to natural gas is probably an anaerobic process, and not a direct result of alkane oxidation (personal communication Michael Henson, R. S. Kerr Lab, U.S. EPA, Ada, Oklahoma).

F. Hydrologic Considerations and Mathematical Modeling of Biorestoration

1. Hydrologic Considerations

A number of methods have been reported in the literature for the containment of contaminated ground water through hydraulic control or through injection-pumping networks of wells. Biorestoration of a contaminant plume may involve the addition of nutrients such as dissolved oxygen or hydrogen peroxide or the addition of microbes capable of degrading a particular waste. In order for such additions to be successful, it may be necessary to use hydraulic controls to minimize the migration of the plume during the in situ treatment process. Thus, hydrologic considerations cannot be neglected in the biorestoration of aquifers.

Hydraulic control methods depend to a large extent on variability of aquifer hydraulic conductivities, background velocities, and sustainable pumping rates. Typical patterns of wells which are used to provide hydraulic controls include: 1) the injection-production pair, 2) a line of downgradient pumping or recharging wells, 3) a pattern of injection-production wells around the boundary of a plume, and 4) the "double-cell" hydraulic containment presented by Wilson (1984). Well systems can also be used to capture and withdraw entire zones of contaminated water for treatment above ground.

Analytical equations and graphical solutions are available for estimating flow rates and limits of hydrodynamic isolation under various boundary conditions. Numerical computer models of ground water flow and contaminant transport are required when site geology is complex, heterogeneous, and anisotropic. A simple hydrodynamic isolation system within a uniform flow field involves the placement of a recharge well of the same strength upgradient from a pumping well. Standard equations describe the head $h(x,y)$ as a function of pumping rate, ambient flow rate, and transmissivity of the aquifer. The region of recirculation which connects the stagnation points can be evaluated, and provides a measure of the capture zone of contaminated ground water (Bear, 1979).

Wilson (1984) presents a "double-cell" hydraulic containment system which utilizes an inner cell and an outer recirculation cell, with four wells along a line bisecting the plume in the direction of flow. The method is more efficient in terms of flushing times and recirculation rates than the single cell. The double-cell method provides added flexibility and a back up system if pumps should fail in either system.

Ozbilgin and Powers (1984) described hydrodynamic isolation systems for several EPA hazardous waste sites. Pumping wells and an upgradient recharge trench were successful in retarding the advance of a contaminated plume at the site in Nashua, New Hampshire. They concluded that hydrodynamic isolation systems are generally less costly and time-consuming than physical containment structures, such as slurry walls. Well systems are more flexible in that pump rates and well locations can be altered as the system is operated over a period of time.

Shafer (1984) indicated that pumping-injection systems can be used 1) to create stagnation (no flow) zones at precise locations in a flow field, 2) to create gradient barriers to pollution migration, 3) to control the trajectory of a contaminant plume, and 4) to intercept the trajectory of a contaminant plume. However, the determination of pumping rates to achieve a pollution control objective can be difficult. Thus, investigators have explored the application of optimization theory to determine optimal pumping rates for creation of hydraulic controls.

Gorelick (1982) and Atwood and Gorelick (1985) focus on using linear programming (LP) methods to determine the best containment strategy in combination with a ground water flow simulator. From a specified set of potential well sites, the model approach selects the best wells and optimal pumping/recharge rate schedules to contain the contaminant plume. Shafer (1984) advocates the use of non-linear programming combined with a ground water flow model and an advective transport model. The optimization method is applied to examples for determing stagnation points in a flow field and for steering the trajectory of a contaminant plume. Optimization methods offer more efficient solutions than the typical trial and error approaches for exploring cleanup strategies. However, nonlinear programming requires the flow and transport models to run during each iteration in which new pumping rates are selected and tested in the overall performance index or objective function. In the present case, optimization methods are complex and time consuming and may not offer any improvements over simulation for the complex case of biorestoration alternatives.

Successful biorestoration alternatives at a particular site depend on the hydrologic and geologic characteristics of the aquifer. If the contaminant plume is moving rapidly through a sandy-gravelly zone, then hydraulic controls may be required to halt the advance of the plume and to provide injection points for added nutrients or oxygen. Pumping out ground water and surface nutrient additions prior to reinjection may provide a more controlled input to the biorestoration process.

For the case of slowly moving organic plumes in a silty sand aquifer, it may be hydrologically difficult to pump or inject recharge waters at rates greater than 5 or 10 gpm. In such cases, large numbers of wells may be needed to provide better "hydraulic spreading" of treated recharge water. Simple lines of wells upgradient or downgradient

63

of the plume may not provide the required circulation, and wells within the plume are usually needed. Five spot patterns (one injection surrounded by four pumping wells) provide a useful network for many cases.

In summary, hydraulic controls for the containment of ground water should be carefully considered for any site where biorestoration is a viable treatment alternative. In particular, injection-pumping well networks offer advantages for the creation of stagnation (no-flow) zones or for the control of the trajectory of a contaminant plume. Once the plume has been controlled hydraulically, then application of additional nutrients, oxygen, or microbes can be better controlled and evaluated in terms of biodegradation efficiency.

2. Modeling Biorestoration

Mathematical modeling of biorestoration processes is useful in simulating cleanup progress and can provide insights into the kinetics of the restoration process. Modeling of the hydraulics of the site may also aid in designing the optimum injection and production system. Development of mathematical models of the biorestoration process requires: 1) a description of the kinetics of biodegradation/transformation in the subsurface; 2) a description of the abiotic processes controlling the transport and availability of the contaminant and other required nutrients; and 3) an appropriate procedure for combining the processes and predicting the effect of the biorestoration technique. Most attempts at quantifying the transport and removal of contaminants in ground water have relied on a solution of the classical form of the advection-dispersion equation. The general form of this equation is

$$\frac{\partial C}{\partial t} = \nabla \cdot (D\nabla C - vC) + \sum R_i \qquad (2\text{-}2)$$

where

C = contaminant concentration

t = time

v = velocity vector

D = dispersion tensor

R_i = chemical and biological reaction terms

Δ = the del operator

Solutions to this equation have been obtained using a variety of analytical and numerical methods. Thorough reviews of these methods may be found in Anderson (1979), Bear (1979) and Javandel et al. (1984). In this section, mathematical descriptions of biodegradation kinetics are reviewed along with commonly used descriptions of abiotic transport processes. Commonly used techniques for solving these equations are then reviewed as well as some of the advantages and disadvantages of mathematical modeling.

3. Kinetics of Biodegradation

In situ biorestoration usually involves the addition of electron acceptors and nutrients to enhance the growth of microorganisms present in the subsurface and consequently increase the rate of contaminant biodegradation. In order to model the degradation process, relationships are needed which describe the kinetics of microbial growth and consumption of added nutrients and electron acceptors. These relationships are then combined with Equation 2-2 to describe the movement and consumption of the contaminant and added nutrients. One of the most popular relationships for describing the growth and decay of microorganisms and consumption of organic substrate was originally proposed by Monod (1942) and modified by Herbert (1956). This model takes the following form:

64

$$\frac{dX}{dt} + \mu XY \ \frac{S}{K+S} - bX \tag{2-3}$$

and

$$\frac{dS}{dt} = \mu X \ \frac{S}{K+S} \tag{2-4}$$

where

X = microbial concentration (mg/L)

μ = maximum specific utilization rate (1/day)

Y = microbial yield coefficient (g/g)

S = limiting substrate (mg/L)

b = microbial decay rate (1/day)

K = substrate half saturation constant (mg/L)

Growth is assumed to be a hyperbolic function of some limiting nutrient. Microbial decay is assumed to be a constant independent of other environmental conditions. When several compounds are used simultaneously, Equation 2-3 can be modified as

$$\frac{dX}{dt} = \mu YX \ \frac{C_1}{K_1 + C_1} \ \frac{C_2}{K_2 + C_3} \ \frac{C_3}{K_3 + C_3} \ \cdots \ \frac{C_n}{K_n + C_n} - bX \tag{2-5}$$

where

C_i = limiting nutrient i

K_i = substrate half saturation constant for nutrient i

When $C_i >> K_i$, the function $(C_i/K_i + C_i)$ goes to 1.0 and has no effect on the growth of the microorganisms, but when $C_i << K_i$, the growth rate will be directly porportional to the concentration of nutrient i. These equations also predict that as the concentration of nutrient i decreases, the net growth rate will approach zero and eventually become negative. For a population to survive, the long term growth rate must be greater than or equal to zero; consequently, the concentration of any limiting nutrient i may not fall below some minimum (C_{min}) where

$$C_{min} = \frac{K_i b}{\mu Y - b} \tag{2-6}$$

This equation suggests that microorganisms may not be capable of degrading organic contaminants below this concentration. McCarty (1985) has suggested the addition of a second non-harmful substrate to support the growth of the organisms and allow degradation to below C_{min}; a more readily degradable substrate could suppress the degradation of contaminant of interest. Yoon et al. (1977) have presented a mathematical model for simulating growth of a mixed microbial population on multiple substrates. For two substrates:

$$\frac{dX}{dt} = \mu^* X - bX$$

(2-7)

where

$$\mu^* = \frac{u_{m1} S_1}{K_1 + S_1 + a_2 S_2} + \frac{u_{m2} S_2}{K_2 + S_2 + a_1 S_1}$$

where

$S_{1,2}$ = substrates 1 and 2

$K_{1,2}$ = half saturation constants for substrates 1 and 2

$u_{m1,m2}$ = maximum specific growth rates for substrates 1 and 2

$a_{1,2}$ = inhibition constants

This model can be further extended to describe growth on multiple substrates.

Some contaminants will not be used as a carbon and energy source by the microorganisms but are transformed. Schmidt et al. (1985) have shown that transformation of these compounds is proportional to microbial population and contaminant concentration (C) where

$$\frac{dC}{dt} = -\mu XC$$

(2-8)

Schmidt et al. (1985) used a logistic curve to describe the change in microbial concentration in a batch system and developed a series of equations for describing change in contaminant concentration with time for differing initial microbial and contaminant concentrations. Use of the logistic curve greatly simplifies the mathematical computations but does not allow simulation of the effects of changing aquifer parameters such as the addition of a second substrate. In aquifer restoration, simulation of the microbial population using Equation 2-3 and change in contaminant concentration by Equation 2-8 may provide a more useful prediction.

Various workers have suggested that the kinetics of microbial growth, decay and consumption of organic contaminants in the subsurface are best described by models which include terms for transport into attached biofilms or microcolonies. It is well known that most microorganisms in the subsurface are attached to soil particles (Harvey et al. 1984). This is thought to be due to the competitive advantage attachment gives a microorganism at low substrate concentrations (Heukelekian and Heller, 1940).

Workers at Stanford University have developed a series of models for simulating degradation of organics in biofilms. The basic model assumes that degradation within the biofilm can be described by Monod kinetics. Mass transport into the biofilm is by diffusion alone. The diffusive flux (J) is calculated from Fick's second law

$$J = -D \frac{dS_f}{d_z}$$

(2-9)

where

S_f = concentration of rate limiting substrate

z = coordinate orthogonal to biofilm

D = diffusivity

Different diffusivities are assigned to the biofilm and an effective diffusion layer adjacent to the biofilm. Williamson and McCarty (1976) originally developed this model to simulate either substrate or oxygen limited biodegradation in wastewater treatment biofilms. Rittman and McCarty (1980) modified this approach to describe the steady state biofilm surrounding an injection well receiving tertiary treated wastewater. Bouwer and McCarty (1984) have further expanded the approach to allow simulation of secondary utilization of trace organics while the biofilm is supported by an undifferentiated chemical oxygen demand (COD). Most recently, Kissel et al. (1984) have employed the biofilm concept to model carbonaceous oxidation, nitrification and denitrification within a mixed culture biofilm.

Much of the work on biofilms at Stanford occurred as an outgrowth of field studies on organic degradation near an injection well. In this region, substrate fluxes and ground water velocities will be high and a biofilm can be expected to develop. Actual biofilms are rare in most aquifers and the majority of the microorganisms are present as microcolonies. Molz et al. (1986) have recently modified the biofilm concept to describe the growth and decay of microorganisms present in microcolonies. An average colony radius and thickness is used to describe the microcolonies. Growth and decay within the colony is simulated by Monod kinetics and includes both oxygen and substrate limitation. Transport to the microcolony is limited by a diffusion layer at the colony surface.

4. Modeling Subsurface Transport

Keely et al. (1986) present a concise overview of evolving concepts of subsurface contaminant transport. They argue that state-of-the-science methods may cost more at the outset, but may yield overall benefits in the form of reduced clean-up costs conpared to conventional methods. The authors make the point that ground water processes are difficult to understand and to model due to interactions which may not be simple to describe. Biotransformations in the presence of dissolved oxygen in an aquifer represents an example where research results may pave the way for reduced clean up costs at many sites. If more detailed data can be obtained about potential pathways and mechanisms of transport, the state-of-the-art will be advanced along with the potential for less costly site restoration.

The major physical processes of importance in ground water transport are advection and dispersion (Freeze and Cherry, 1979). Advection is the transport of a contaminant by the bulk ground water flow. Dispersion is the spreading of a contaminant front due to molecular diffusion and small scale variations in fluid velocity throughout the aquifer.

The major chemical processes of interest are adsorption, ion exchange, hydrolysis, and oxidation-reduction reactions. Adsorption is "the process in which matter is extracted from the solution phase and concentrated on the surface of the solid material" (Weber, 1972).

Dispersion--

Dispersion, the spreading of a contaminant front as it moves in the ground water, is an area of particular controversy at this time. The dispersion process can be most easily described as consisting of three components: 1) molecular diffusion resulting from Brownian motion of individual molecules; 2) hydrodynamic dispersion resulting from variations in interstitial pore velocities; and 3) macrodispersion resulting from structural variations in hydraulic conductivity and, consequently, in velocity. Differences in permeability between layers can result in different ground water velocities and large variations in solute concentration. When an aquifer is monitored using a fully screened well, ground water from different layers is mixed, resulting in a smoothing of the apparent solute

breakthrough curve. This smoothing can result in very large apparent dispersion when matched against simple two dimensional solute transport models.

The effects of molecular diffusion, hydrodynamic dispersion and macro-dispersion are frequently combined to form a dispersivity tensor which in some cases can be reduced to three main components: longitudinal dispersivity (a_1), transverse dispersivity (a_t), and vertical dispersivity (a_v). Dispersion coefficients (D) used in the advection dispersion equation are found by

$$D = av^m \qquad\qquad (2\text{-}10)$$

where

v is the resultant velocity scalar

m is assumed equal to 1.0

The physics and mathematics necessary to describe molecular diffusion and hydrodynamic dispersion are well established. Bear (1979) and Fried (1975) provide comprehensive experimental and theoretical reviews of these processes. The significance of the third component, macrodispersion, is the subject of much debate. Anderson (1981) summarizes much of the current research on the nature and significance of macrodispersion. At present there appears to be two dominant approaches.

1. Macrodispersion occurs due to random variations in permeability which can never be adequately characterized; consequently, the only reasonable method is to employ a stochastic procedure for describing the average movement of a solute; or
2. The apparent spreading of many solute fronts is due to variations in permeability which are complex but measureable; consequently, more effort should be expended towards measuring the actual permeability distributions and using these as input for deterministic simulations.

No work has yet been focused on the effect of varying aquifer parameters on solute transport as it relates to biorestoration. At present, the predictive accuracy of biorestoration modeling is severely limited by uncertainties in solute transport simulations. When simulating the transport of a contaminant and oxygen or other nutrient, the most commonly used numerical models will predict significant mixing between the contaminants and oxygen and high rates of biodegradation. In real aquifers, contaminants may be trapped in a few areas of low permeability while the oxygen or other nutrients are forced through the high permeability zones. In this situation, little mixing of the contaminant and oxygen will occur, and consequently, little biodegradation. Until solute transport models are developed which can adequately describe the complexities of subsurface flow, the accuracy in which biorestoration can be simulated will be limited.

Chemical Processes--

The major chemical processes which affect the transport of organic contaminants in ground water are adsorption and hydrolysis.

Adsorption is a surface process in which a compound "sticks" to the solid aquifer material. In the case of neutral, nonpolar organics, this stickiness is due to the much higher affinity of the compound for other organics attached to the soil than for the polar water phase. In the case of polar molecules, adsorption may be due to dipole:dipole forces. The attraction due to this mechanism is typically much weaker than that for hydrophobic compounds.

Naturally occurring organic material in aquifers is commonly present as a humic-kerogen film over the clay particles. This organic material may originate from humic or fulvic acids deposited with the original sediment or from infiltrating rain water. Organic material is effectively preserved in tight clays where diffusion of oxygen is limited and the redox potential is low.

68

Hydrolysis reactions can have a major impact on the mobility of organic compounds in aquifers. These reactions are typically pH dependent and catalyzed by metal ions. The pH of most solutions will approach equilibrium shortly after entering an aquifer. In this case, hydrolysis reactions can be modeled as a simple first order decay process.

When attempting to develop models for simulating the adsorption of contaminants in ground water, many early investigators assumed that at low concentrations, contaminants move independently of other solutes, the reaction kinetics are fast relative to ground water flow and the natural reactants are uniformly distributed throughout the aquifer. These assumptions allow the reactions to be analyzed using the equilibrium isotherm approach. Under this approach the variation in adsorbed contaminant concentration is described by an adsorption isotherm:

$$S = f(C) \tag{2-11}$$

where C = concentration of the contaminant in solution and S is the concentration in the nonmobile solid phase. This relationhip can be incorporated into the advection dispersion equation by considering the loss of solute to adsorption.

If S is a linear function of C then the effect of adsorption can be replaced by a constant retardation factor (R). In this special case the adsorbed contaminant will move according to Equation 2-2 with an effective velocity, v', where v' = v/R and an effective dispersion coefficient, D' = D/R. A common method of calculating R is by the relation (Freeze and Cherry, 1979).

$$R = 1 + n \ K_d / \rho \tag{2-12}$$

where n is the aquifer porosity, p the bulk density, and K_d the partition coefficient in grams of contaminant adsorbed per gram aquifer.

The use of a retardation factor depends on the following assumptions:

1. Adsorption can be described by a linear relationship between solute and solid phase concentration.
2. The reaction kinetics are fast relative to ground water flow.
3. Natural reactants attached to the aquifer material can be assumed uniformly distributed in space.
4. Contaminant transport is independent of other liquid phase organics.

5. Mathematical Models of Subsurface Biorestoration

Equation 2-2 with terms included for biodegradation can be solved to obtain the concentration of the contaminant in space and time by both analytical and numerical methods. Analytical solutions generally require less effort for the model user to employ, but may also require simplification of the aquifer conditions and biodegradation processes. For uniform flow in an aquifer in which biodegradation may be approximated as a first order decay, solute concentrations in space and time can be calculated using the one dimensional solution of Ogata and Banks (1961) or the two dimensional solution of Wilson and Miller (1978). Approximating biodegradation as a first order decay would be appropriate when the microbial concentration is constant, growth is only dependent on the contaminant concentration, and the contaminant concentration is significantly less than the half saturation constant (K). Simkins and Alexander (1984) provide useful guidelines for determining when consumption of substrate may be approximated as a first order decay.

Numerical solution of Equation 2-2 allows the user much more flexibility in specifying aquifer geometry and biodegradation kinetics. The most common mathematical formulations for approximating the solute transport equation are finite differences, finite elements, and the methods of characteristics.

Finite difference models have been developed for a variety of field situations including saturated and unsaturatd flow, and for transient and constant pollutant sources. Finite difference methods operate by dividing space into

rectilinear cells along the coordinate axes. Homogeneous values within each cell are represented by values at a single node. Partial differentials can then be approximated by finite differences and the resulting set of equations solved by iteration (Mercer and Faust, 1981; Prickett, 1975). Approximating the differentials by a difference requires that the remaining terms of the Taylor's expansion be dropped resulting in a truncation error and signficant spreading of the simulated contaminant front. This spreading has been termed numerical dispersion and can often mask the actual physical dispersion process (Anderson, 1979).

The finite element method also operates by breaking the flow field into elements, but in this case the elements may vary in size and shape. In the case of a triangular element, the geometry would be described by the three corner nodes where heads and concentrations are computed. The head or concentration within an element is allowed to vary in proportion to the distance to these nodes. Complex interpolating schemes are sometimes used to predict parameter values accurately within an element and thereby reduce the truncation errors common in finite difference procedures. Some numerical dispersion may still occur but is usually much less significant. The use of variable size and shape elements also allows greater flexibility in the analysis of moving boundary problems which occur when there is a moving water table or when contaminant and flow transport must be analyzed as a coupled problem. A disadvantage of the finite element method is the greater mathematical complexity and generally higher computing costs (Pinder and Gray, 1977; Wang and Anderson, 1982).

The method of characteristics (MOC) is most useful where solute transport is dominated by convective transport. One of the most commonly used models employs a procedure where idealized particles are tracked through the flow field (Konikow and Bredehoeft, 1978). In step one, a particle and associated mass of contaminant is translated a certain distance according to the flow velocity. The second step adds on the effect of longitudinal and transverse dispersion and sources and sinks for the contaminant.

All of these techniques can be used to simulate in situ biorestoration under certain circumstances although no single procedure will be applicable to every situation. Only very limited work has been done on simulating the simultaneous effects of advection, dispersion, and chemical and biological processes. In the following section, the few studies that have been performed are reviewed and the potential weakness of each technique discussed.

Kosson et al. (1985) employ a simple one-dimensional finite difference solution to simulate the movement of hazardous industrial wastewaters through an acclimated soil column. Adsorption is assumed to be linear and is described by a retardation factor. A portion of the influent wastewater is assumed nondegradable. Biodegradation of the remainder is simulated as a first order decay. Experimental data are also provided by a field scale column used to study the degradation process. The model adequately matches experimental data from the later portion of the column biodegradation test when an acclimated microbial population had developed. Agreement between model and experimental results is not as good during the earlier part of the test before the microbial population had reached steady state.

Angelakis and Rolston (1985) present a mathematical model for simulating the movement of insoluble (particulate) and soluble organic carbon through the unsaturated soil profile. Transformation from insoluble to soluble and finally to carbon dioxide is assumed to follow first order kinetics. Transport of carbon dioxide is by gaseous diffusion. Simulation results are obtained from analytical and numerical solutions. These results compare favorably with experimental data from a series of column tests performed using primary wastewater effluent. Insoluble and soluble organic carbon distributions were adequately matched. A variable gaseous diffusion coefficient was required to match the observed carbon dioxide distribution.

Baehr and Corapcioglu (1985) present a one dimensional model for simulating gasoline transport in the unsaturated zone which includes transport by air, water, and free hydrocarbon phases. The hydrocarbon is assumed to be composed of n components of differing solubility and volatility. Exchange between the air, water, hydrocarbon and adsorbed phases is assumed to be rapid and described by equilibrium partition coefficients. Biodegradation of the hydrocarbon is limited by the availability of oxygen which can enter the soil dissolved in the water phase or by gaseous diffusion. Microorganism growth was not simulated directly since biodegradation was assumed to be rapid relative to mass transport and to be limited by the availability of oxygen. The equations are solved numerically using a finite difference procedure. Model simulations indicated that the rate of

70

biodegradation was very sensitive to the diffusive properties of the soil. No experimental data are presented to test the model predictions.

Sykes et al. (1982) simulate the anaerobic degradation of a landfill leachate plume in the saturated zone at the Canadian Forces Base in Borden, Ontario. Microbial growth, decay and substrate utilization are simulated using Monod kinetics. When substrate concentrations are significantly below the half saturation constant and microbial populations are close to steady state, the biodegradation kinetics are reduced to a first order decay. The nonlinear equations are generated using a Galerkin finite element approximation and solved using a Newton Raphson iteration procedure. Model simulations indicate that the majority of the degradable organics can be expected to be removed within a few meters of the landfill. This finding was confirmed in field studies at the site. Sensitivity analyses performed using a one dimensional solution indicated that under certain circumstances, pulses of organics could escape from the landfill before a significant microbial population has developed.

Molz et al. (1986) present a numerical model for simulating substrate and oxygen transport and use by attached microorganisms. The microbial population is assumed to be immobile and present in microcolonies of an average thickness and radius. Transport into the microcolonies of oxygen and substrate is limited by diffusion through a stagnant layer adjacent to the microcolony. Microbial growth and consumption of oxygen and substrate within the microcolony is described by Monod kinetics. A one dimensional solution is obtained numerically using an Eulerian-Lagrangian finite element solution. The numerical model will be then used to simulate the transport and biodegradation of substrate and oxygen in a laboratory column. The simulation results indicate that degradation is most rapid near the column inlet. The initial microbial population has a significant effect on the simulated breakthrough at the beginning of the simulation but has little effect on the steady state substrate distribution. Large substrate loadings at the column inlet quickly exceed the available oxygen supply resulting in anaerobic conditions throughout the majority of the column. Laboratory testing of the simulation model is planned.

Borden and Bedient (1986) present a numerical model of oxygen limited biodegradation of hydrocarbons in the saturated zone. Numerical solutions are obtained by approximating one dimensional flow as a series of completely mixed reactors and two dimensional flow using an explicit finite difference solution corrected for numerical dispersion. One dimensional model simulations indicate that biodegradation will be very rapid near the contaminant source when oxygen is present. When no oxygen is present at the source, biodegradation will be slow and limited by the transport of oxygen into the contaminant plume. Two dimensional simulations indicate that horizontal and vertical mixing are the major sources of oxygen to the contaminant plume and control the biodegradation process. When adsorption of the hydrocarbon to the aquifer is significant, advective fluxes of oxygen into the plume and resulting biodegradation is also significant. Sensitivity analyses with the model suggest that for many aquifers, the reaction between oxygen and hydrocarbon may be approximated as an instantaneous reaction since oxygen transport is rate limiting. Borden et al. (1986) employ these results to modify the USGS Solute Transport Model (Konikow and Bredehoeft, 1978) to simulate oxygen-limited biodegradation of creosote wastes at a Superfund site. The model gave an adequate description of the observed oxygen and hydrocarbon distributions in the shallow aquifer at the site and was used to study various remedial actions including no action and removal of the contaminant source.

Dawson et al. (1986) modify a petroleum reservoir code to simulate enhanced in situ biorestoration using the equations presented by Borden and Bedient (1986). Advective and dispersive transport is calculated using a finite element-modified method of characteristics solution which allows a large time step and strongly advection dominated flow. Because the rates of biodegradation can be very high relative to transport, a time splitting scheme is employed where the microbial kinetic terms are solved separately using an implicit solution with a much smaller time step. This model is then employed to simulate enhanced in situ biorestoration by the injection of oxygen and production of contaminated water by a five-spot pattern. Simulations are performed for a variety of conditions including uniform and random permeabilities and variable adsorption.

6. Model Use and Limitations

The current technology for simulating subsurface biorestoration is still in its infancy. Some progress has been made in developing kinetic descriptions of the biodegradation process and combining these with available solute

transport models. Unfortunately, little reliable field data has been available to rigorously test these models. Considerable uncertainty exists over the importance of simulating transport into biofilms or microcolonies. Also, the effects of variations in aquifer parameters on the efficiency of biorestoration is unknown. At present, the technology is not available to quantitatively predict the efficiency of enhanced biorestoration but significant advances are being made in our ability to describe the process.

7. Conclusions

Of the available biological aquifer remediation techniques, the most effective methods are enhancement of the native population and withdrawal and treatment by various wastewater treatment processes (Lee and Ward, 1984). Before any aquifer remediation technique can be implemented, a thorough understanding of the hydrogeology and contamination problems of the site must be obtained and used to design the treatment sytem (Lee et al., 1986). Costs for treatment may range from tens of thousands up to tens of millions, depending upon the extent and nature of the contaminants, the nature of the site, and the desired cleanup levels.

Addition of oxygen, nitrogn, phosphorus, and trace minerals stimulates the acclimated indigeneous microbial population to aerobically degrade the contaminants. In situ biorestoration has been chiefly used to treat gasoline contaminated aquifers, but also has been employed with ethylene glycol and solvents including acetone, tetrahydrofuran, methylene chloride, n-butanol, dimethyl aniline, and isopropanol. Biorestoration effectiveness will be affected by toxic levels of organics and heavy metals. In general, in situ bioreclamation has been effective in reducing the quantity of the contaminants, but not in completely eliminating them. The treatment moves with the plume allowing treatment of trapped or sorbed contaminants or, by using soil flushing or an infiltration gallery, in situ microbial treatment can reach areas that are not accessible by other techniques. Biorestoration has been used in a number of aquifers, but may be of limited usefulness in those with low permeabilities. Undesirable metabolic and inorganic nutrients may escape from the treatment zone and affect ground water or surface water quality. Alternative oxygen sources such as ozone, hydrogen peroxide, pure oxygen, and air flooding or soil venting may speed the removal of the organic contaminants, but their impact on the microbial population and the geochemistry of the site is not fully understood. Innovative processes such as treatment beds or land treatment can be used in some situations. In the presence of an acclimated microbial population, many aquifers will be anaerobic because the microorganisms will have depleted the dissolved oxygen. It will be possible to use anaerobic degradation to remove contaminants, although the technology for this treatment has not yet been developed. Reducing the interfacial tension between the hydrocarbon and ground water with surfactants, dispersants, or emulsifiers will mobilize the contaminants and may make them available for microbial degradation. Combinations of in situ biorestoration treatment with other chemical, physical, or biological treatment processes have been successfully utilized in aquifer remediation.

Treatment by biological wastewater processes is a proven technology. The biological processes include activated sludge, lagoons, waste stabilization ponds, fluidized bed reactors, trickling filters, rotating biological discs, and sequencing batch reactor. All of these processes are dependent upon extraction of the contaminated ground water from the subsurface. Combinations of conventional wastewater treatment processes and other water treatment processes have also been successful.

Alteration of the subsurface microbial community has a great deal of potential to allow degradation of recalcitrant compounds in the subsurface. The added organisms are selected by enrichment culturing or genetic manipulation. However, introduction of non-native microorganisms may be limited by movement of the organisms through the subsurface, survival of the organisms, and accessibility of the organic contaminants. Addition of an acclimated population may be more successful when combined with wastewater treatment processes where the environment can be more closely regulated. Although the aquifer remedial actions that have used a microbial seed have not conclusively shown that the added organisms were responsible for removal of the contaminant, the concentrations of the contaminants were reduced. Alteration of the environment to promote the activity of a particular component of the microbial community is another promising technology. Field tests and further research are currently underway for this technology. The environment is altered to promote the growth of organisms that co-oxidize halogenated aliphatics when supported on gaseous hydrocarbons such as methane, propane, or natural gas.

72

Techniques for simulating the subsurface biorestoration process are under development, but little reliable field data has been generated that can be applied to these models. Some of the major considerations in simulating transport and biodegradation of organic contaminants in the subsurface are poorly understood; these include the importance of transport of organics to the bacteria and the variability in aquifer parameters.

III. Institutional Limitations on Ground Water Pollution Control

The development and application of technologies for the prevention and regulation of leaking underground storage tanks is a complex and interdisciplinary science, as is the abatement and cleanup of the ground water contamination threats such leaks present. This science is further complicated, however, by the institutional limitations that control the rate at which technology can advance and its use in the development of regulations. Institutional limitations may be the factor in determining how the technology will be applied to leaking underground storage tank regulation and remediation. These institutional limitations that control the rate at which technology can advance and its use in the development of regulations. Institutional limitations may be the factor in determining how the technology will be applied to leaking underground storage tank regulation and remediation. These institutional limitations include: (1) the scientific understanding of the nature of leaking underground storage tanks and released products; (2) public opinion; (3) business community attitudes; (4) environmental interest group concerns; and (5) governmental acceptance, use, and implementation of the remedial technology.

A. Scientific Understanding of the Nature of Released Products from Leaking Underground Storage Tanks

Although continuously researched and tested, the scientific understanding of the nature of a released product and its behavior in the subsurface, as well as the causes of leaks in underground storage tanks, is still rather limited. These subjects are being researched in laboratory microcosms and through the use of models, but field conditions continue to produce situations where only limited scientific understanding is available for the development of remedial technologies. These limitations can be described within the following categories: (1) the physical and chemical nature of petroleum products in the subsurface; (2) the nature and occurrence of leaks in underground storage tanks; and (3) hydrogeologic complications associated with the migration of contaminant plumes.

1. Physical and Chemical Nature of Petroleum Products

Petroleum products commonly stored in underground storage tanks are labeled with familiar names such as "regular", "unleaded", and "super-unleaded" gasoline, diesel, and kerosene. While the names infer a single compound, they are misleading in that they actually refer to a very complex mixture of chemicals which can include a variety of hydrocarbons and additives. These multiple components have individual physical and chemical characteristics which can interact and react independently when introduced into the subsurface from a leaking tank. Petroleum products from three separate phases during their migration through soil media and in their contact with ground water: (1) free product phase; (2) dissolved phase; and (3) vapor phase.

The free product phase describes the body of the product which retains its basic identity and composition in the subsurface. The main portion of the contaminant plume meets this description, but so does the residual product which is retained in the subsurface media as the plume is transported away from the leaking underground storage tank. The dissolved phase describes that portion of the released product which goes into solution with contacted ground water. Because the product is a mixture of chemicals, compounds react and dissolve with the ground water based on their individual properties and their individual equilibrium reactions, as well as through the effects of the interacting reactions and combined equilibrium conditions.

73

volatilize from both the free (and residual) product phase and the dissolved phase with concentrations based on both product quantity and individual and combined equilibrium rates.

The three phases also include the portion of the residual product which is inundated as the ground water level fluctuates with rising and falling water tables. A rising water table may dissolve a portion of the residual product as well as floating it to reform free product. A falling water table may cause the reformed free product to again adhere to the subsurface media as a residue. The vapor phase may be evident during this fluctuating process.

The primary scientific limitation involving the nature of the leaked product is associated with understanding, analyzing, and researching interactions of the multitude of compounds present in the petroleum product with the multitude of existing subsurface media. Researching the rates and effects of partitioning, synergistic reactions, volatilization, dissolution, and adsorption for this multitude of compounds is very time consuming and has only fairly recently been intensively undertaken. Analytical characterization of these compounds can be expensive and time consuming, and it is very dependent on current developments in analytical techniques and equipment.

In addition, some components of petroleum products are known to degrade in the subsurface through microbial processes. The study of these processes is critical to the understanding of the fate of petroleum products in the subsurface.

2. Nature of Occurrence of Leaks

Improper installation, corrosion damage, external damage, internal punctures, and rusting of tank bottoms are commonly documented causes of underground tank leakage. While the nature of underground storage tank failures and leaks can be easily determined and are well documented, the actual mechanisms for tank integrity problems are often complex. The physical and chemical processes involved identifying the combined forces which result in a tank collapse or failure are complicated and often do not truly define the cause of a failure.

Improper tank installation or external human activities can cause tank leakage. Undetected non-uniform backfill around a tank, such as a single sharp rock, a piece of metal, and/or irregularly packed backfill, can lead to tank failure. A single lump of clay or a stray current from adjacent businesses, transportation systems, or utilities can produce unexpected and rapid corrosion of underground storage tank system components.

Improper maintenance or system abuse can create conditions which result in tank and piping failure or system deterioration. "Spearing" a tank bottom while checking the tank product level, or bouncing the level indicator device off the tank bottom by inexperienced and unsuspecting operators, can result in immediate tank failure or the weakening of the tank material beneath the fill spout. the lack of water detection in operating tanks and its frequent removal can result in tank bottom corrosion and possible tank failure. Improper maintenance of protective cover pads over the underground storage tank system can result in crushed lines or a collapsed tank due to heavy vehicular traffic over deteriorated areas. These relatively minor and often unseen conditions can easily undermine the best constructed underground storage tank system.

The nature and occurrence of leaks and spills from underground storage tanks is also more complex than is generally believed. Current discussions regarding regulatory requirements to detect leaks often center on the installation of monitoring wells around underground storage tank systems. These wells may even be required to be equipped with hydrocarbon detectors in lieu of periodic sampling. However, what will the detection of hydrocarbons in the monitoring wells tell the underground storage tank system owner or operator? The contamination could come from surface spills at the service islands, transfer spills, overfill spills, or even spills on adjacent or distant properties. The implication that contamination in the wells would clearly indicate a leak in the underground storage tank system could cost the owner or operator a great deal of money for integrity tests, tank or piping removal, additional bore holes or monitoring well drilling, or legal fees. The determination of the source of subsurface hydrocarbons is a critical factor for the implementation of any underground storage tank regulations or the development of remedial technology.

74

The location of the deterioration in the tank can often produce leaked product or sometimes not be a constant environmental threat. If a deterioration occurs in the bottom of the tank or below the lowest maintained product level, a continuous leak can occur. If the deterioration is slight, a leak could occur only when the hydraulic head is great enough to drive the product out of the tank. If a deterioration exists below the highest maintained inventory but above the lowest level, an intermittent leak will occur whose magnitude will be related to the volume of product above the leak. The deterioration may even exist above the highest maintained level and a leak may never occur.

The water table can affect the rate of a leak as well as the existence of a leak. If a tank is inundated by ground water, the flow of product from the tank versus the flow of ground water into the tank is controlled by the pressure difference of each liquid's hydraulic head. If the tank product has a greater head, product can leak out. If the ground water has a greater head, water will enter the tank.

The predictability of tank leaks, and extent of product migration into the subsurface environment, and their remediation are limited to knowing when a deterioration in a tank is acting as a leak source. The prediction of a constant leak from the bottom of a tank is relatively simple and can be simulated with a number of computer models. A sporadic leak is much more difficult to simulate. Such a leak may never reach a magnitude that can even be detected, or it can produce individual spills of varying volumes at widely varying times dependent on inventory volumes.

Pipeline leaks can also be very erratic and hard to predict and evaluate. The types of pumps used in transferring product from the tank to the dispenser directly affect the occurrence of leaks from a pipeline system. A positive head pump pushes the product into the pipeline. If a pipeline leak occurs, the positive pressure on the pipeline forces the product out of the system. A negative head pump pulls the product from the tank to the dispenser. If a pipeline leak occurs, the vacuum created on the pipeline draws air into the system. Although little or no product is lost while the negative pump operates, the pipelines still contain product while the system is passive, as with the positive head system, and product can leak from the system. This erratic loss of product has the same limiting impact on the predictability and evaluation of piping leaks as do the occurrence of leaks from tanks.

3. Hydrogeologic Complications

Once a tank product is introduced into the subsurface from a leak, a detailed understanding of the physical and chemical nature of the contaminant and its interaction with the subsurface, and the local hydrogeologic formations and features through which it migrates, is essential. Any technology developed for the remediation of underground storage tanks must take into account the physical characteristics of the subsurface which dictate the migration path of the contaminants. Unfortunately, the subsurface is not always a homogenous formation with predictable, and reproducible effects on contaminant plume movement. The complexities of lens formations, karst formations, fracture formations, irregular confining beds, perched aquifers, recharge zones, etc., are rather well documented and clearly represent a limiting factor in the development of remedial technologies for leaking underground storage tanks.

Additional limiting factors in the development of remedial technologies are unnatural features present around underground storage tank systems which affect the fate of leaks from these systems. These factors include: (1) the fill material surrounding tanks and pipelines; and (2) underground utility and service lines and their associated backfill. Backfill material varies around underground storage tank systems from pea-sized gravel to original excavation material, from similar backfill around the entire underground system to one type of backfill around the tanks of a system with a different type around the pipelines, from old tanks or piping having original excavation material backfill to new or replacement tanks or lines having imported backfill, etc. The older the underground storage tank system, the more variable the backfills and inconsistencies which can be expected around each component of that system.

If a tank has a backfill that is more permeable than the subsurface surrounding the excavation, leaked product can pool within the excavation and migrate into the environment following a path of least resistance. The product might overflow the excavation and migrate along the land surface or along road foundations or into adjacent

building backfills. The product might pool until it migrates vertically through the underlying strata. The product could even pool within the excavation and act as a hydraulic seal preventing additional product from leaking out of the tank.

If a tank has a backfill that is less permeable than the surrounding material, the migration of the leaked product can be, at first, held intimately to the tank's external surface until the backfill becomes saturated and the product breaks through to the surrounding subsurface material. Once the product breaks through, its migration is controlled by the characteristics of this subsurface material.

Once product migrates away from the tank excavation, it can be intercepted by utility and service lines such as sanitary sewer lines, storm sewer lines, water lines, telephone service lines, natural gas lines, etc. The migrating product can follow these lines using surface tension or, if the backfill of the lines is more permeable than the natural substrate, can preferentially follow a line with a large portion of the contaminant plume becoming involved. As the product migrates along the lines, it can degrade seals or the line material itself, and can cause extensive damage or enter the line system. If the line is a sanitary sewer line, the product can appear in toilets or sinks a great distance away from the leak source without affecting hook-ups between the source and the surfaced product. If the line is a water line, the contamination can be widespread with a variety of effects. Telephone service lines and manholes can become storage structures for leaked product, not being discovered until service problems arise and the service personnel attempt to enter the manhole.

These unnatural features can divert the migrating plume along very erratic and unexpected routes. They present themselves, in certain situations, as radical limiting factors in the development of remedial technologies for underground storage tanks.

B. Public Opinion

A very large portion of the public owns automobiles and relies heavily on petroleum products. Therefore, awareness of the problem of service station leaks and the forthcoming regulations is fairly common. Public opinion towards the development and implementation of underground storage tank programs can be grouped under three headings: (1) persons not generally concerned with, but who will openly accept the forthcoming regulations due to either apathy, ignorance, or having a clear understanding of the need for such regulations; (2) persons concerned about increasing government control over and interference with private industry; and (3) persons who have been affected or who fear they will be affected by leaking underground storage tank incidents.

A portion of the public will accept forthcoming underground storage tank regulations because they feel that they will not be very affected by them. They will be willing to accept increased costs for petroleum which may occur with the new requirements, or they may not yet be aware that higher costs may result. They may have heard of the problems with leaking underground storage tanks and realize the need to remedy the potential threat. The apathetic portion of the public may not realize the potential commercial impacts of such regulations, or they may feel that such impacts are acceptable. A large group may well understand the problems related to leaking underground storage tanks and will openly accept any programs and associated impacts in order to control the potential and existing threat.

Another portion of the public is very concerned over increased governmental control over private industry, thus they consider attempts to regulate this problem as interference. They feel that the industry can take care of itself. This group would include a large portion of the small station owners and related businesses who may not be able to survive stringent regulations. They look at past government involvement with farmers, the past oil embargo, and the history and related press involving price controls, wheat subsidies, etc., and fear government involvement. They especially fear the potential impact on small businesses and the common fear of the "rich getting richer and the poor getting poorer". The recent economic condition of the country fuels these fears as they see that it gets harder and harder for small businesses to survive. The concerns of this portion of the public are very real and must be considered as the technology is developed for the remediation of leaking underground storage tanks, and the forthcoming underground storage tank programs and associated regulations.

76

A growing portion of the public, although thankfully still a minority, are those who have been affected by leaking underground storage tank incidents or know of persons who have been affected. These people have lost their water wells, have had their water supplies contaminated, have had flammable fumes enter their homes or businesses, or have lost property due to explosions or extensive contamination. Others have lost their businesses due to exorbitant clean-up costs for leaks they are legally responsible for, have paid exorbitant legal fees when they have been sued for damages, pay higher and higher insurance, have had to pay for new water wells, or have lost farms or homes because they could not find an uncontaminated water supply after theirs was lost due to leaking underground storage tanks. Still others feel they have been given the runaround by the government to which they have gone for help. They feel exasperated because no one is able to solve the contamination problem which has crept beneath them. They feel helpless as their health worsens and their lives fall apart as a result of drinking undetected contaminated water, or as they breathe fumes from leaked products. These persons will probably have the greatest public voice in the development of leaking underground storage tank remedial technologies and underground storage tank programs.

C. Business Community Attitudes

The business community and their general attitudes towards the development and implementation of underground storage tank programs can be grouped into four categories: (1) underground storage tank owners and operators, including retail businesses and companies which maintain their own underground storage tank systems not for retail sales use; (2) insurance companies; (3) petroleum product sales support and maintenance companies; and (4) the general business community.

1. Underground Storage Tank Owners and Operators

Underground storage tank owners and operators will be the group most affected by underground storage tank regulations. This group includes refineries, chemical plants, and retail stations as well as other businesses which maintain underground storage tanks for vehicle fleets such as bus companies, ice companies, automobile dealerships, etc. Even local, state, and federal government entities maintain underground storage tanks for vehicle fleets. The concerns of the underground storage tank owners and operator fall into three main areas: (1) is their system currently leaking and how can they adapt to new requirements; (2) can they financially survive such regulations; and (3) can the government develop regulations that solve the problem without going to extremes?

When asked, most owners and operators will emphatically state that their underground storage tank system is not leaking. An alarmingly large number of small business operators, however, do not keep adequate inventory records and are often not aware of the signs that their system may not be tight. They know that if the system is leaking, the financial outlay to correct the problem will probably put them out of business. Without adequate funds, survival of the business relies on hoping the system is tight. Larger companies that have adequate funds for system and component testing, repair, and replacement will quickly provide proof of system tightness or take appropriate action to remedy a leaking system.

Small businesses fear the implementation of underground storage tank programs because current economic conditions have severely limited their profits. If required, these businesses could not afford to provide proof that their system is tight, and would probably go out of business long before they were required to retrofit their system with leak protection or detection. These businesses realize that regulations are being developed, realize that they may not survive, but will continue to operate while they can. Owners of these businesses will probably oppose the implementation of regulations but realize their survival is short-lived.

Larger, privately owned stations can usually afford to adequately maintain their underground storage tank systems, keep close watch of their inventory, investigate possible signs of leaks, and make necessary repairs, replacements, and cleanups when necessary. These businesses are more concerned over how strict the regulations will be, and how they will have to alter their operation to survive. They realize that it takes money to maintain an underground storage tank and a business and they are, hopefully, making enough profit to adapt to forthcoming underground storage tank program requirements.

Currently, corporation-owned stations are generally already implementing programs that they perceive an underground storage tank program might include. They realize that by the time the regulations are implemented, inflation will cause the installation of required leak prevention and detection equipment to cost a great deal more than they would now. They also feel that, because of their size, own staff expertise, and potential lobbying capabilities, they can convince regulators that their systems are tight and well-protected. They may however, fear for their survival should the new regulations be more stringent than they have anticipated.

Also in response to the forthcoming regulations, major oil companies are cutting back on the number of stations they operate. Many stations are being sold. The buyers of these stations are very aware of the potential problems with such stations, and are requiring site contamination evaluations prior to the sale as a condition of the sales agreement. The sale of these stations lessens the chances for pollution liability over time for the seller by getting rid of sites which may be considered high potential pollution risks. Buyers must realize this and be willing to make the necessary improvements to abate risk once the site has been shown to be clean or has been cleaned up.

A major concern of all underground storage tank owners is the ability of the government to develop reasonable regulations in its rush to regulate underground storage tanks and get control of the leaking underground storage tank problem. Large businesses are concerned about their international competitiveness if regulation becomes excessive. Small businesses are very concerned that the developing regulations may not consider the smaller, privately owned stations and small oil companies. Small businesses rely on petroleum marketing associations to actively lobby state and federal governments in an effort to assure reasonable regulation development. Large oil companies, in addition to their lobbying efforts, are sponsoring or co-sponsoring, with consulting firms and related associations, educational seminars on the prevention of leaking underground storage tanks, maintenance of underground storage tanks, and existing state and local regulation of underground storage tanks. These seminars can help educate government employees so that reasonable and intelligent regulations can be developed.

2. Insurance Companies

An additional factor that all underground storage tank owners are concerned about is having adequate insurance coverage in case a leaking underground storage tank incident occurs. The concern is greater in smaller businesses, but still exists even in the large corporations. Insurance companies are also very concerned with this problem. In recent years the number of leaking underground storage tank incidents has dramatically

increased. Technology has developed to analyze the impacts of the associated contamination, but the costs of incident evaluation, abatement, and remediation can be extensive. As insurance companies have had to pay out more and more for these episodes, policies are now being cancelled, greater restrictions are being placed on policies that are issued, and the cost of insurance is soaring.

In an effort to control costs, an increasing number of insurance companies are contracting their own environmental consultants to cleanup leaking underground storage tank incidents experienced by policy holders. The consultants are also contracted to drill monitoring wells at most stations of policy holders to detect leaks before the cost of handling a pollution incident become even more expensive. This concern for cost control includes a concern that governmental bureaucracies can develop reasonable and adequate regulations which can help stem the number of leak events and, thereby, lessen the number and related expenses of policy claims.

3. Petroleum Product Sales Support and Maintenance Companies

Another business group which can be directly affected by underground storage tank programs is the petroleum product sales support and maintenance companies. If the forthcoming regulations force stations out of business, these companies could realize a major loss of business. However, these businesses could realize an increase in business by dealing in leak prevention and detection equipment. The economic hard times for retail stations can also increase the wholesale business of service-related products as stations sell additional products to increase profits.

This group of businesses often deals in state-of-the-art leak prevention and detection products which can result in high business risks. Not all of the products currently on the market have been adequately tested, proven to perform their advertised claims, been proven to work adequately through time, or been tested as having a potential for showing false readings. If regulations are implemented which restrict the use of uncertified equipment or require certain minimum standards which stockpiled detection or prevention equipment do not meet, wholesale or service businesses could be as adversely affected as underground storage tank owners. Currently, governmental bureaucracies provide little or no guidance or control for this type of equipment. As a result, these support businesses, which operate on a demand basis, have great interest in and concern over the development of underground storage tank regulations.

4. General Business Community

In addition to the petroleum-related businesses, the general business community also has concerns over the development of underground storage tank regulations. Private business is wary of government involvement in private industry. They often resent additional governmental control over problems which could be handled by an industry itself. They see increased costs resulting from such involvement.

D. Environmental Interest Groups

Environmental interest groups are very aware of the existing and potential problems with leaking underground storage tanks. They understand the toxic and carcinogenic nature of petroleum products and the impact that these compounds can have in the environment. They see the immediate need for the development and implementation of underground storage tank programs, but doubt the government's ability to perform the task.

These groups are concerned that inadequate regulations may be implemented because the government is unaware of the severity of the problem. They are concerned that the forthcoming regulations may not require enough safeguards on underground storage tank systems due to lobbying efforts by big business. The final requirements may also tend to give preferential treatment to big business due to these strong lobbying efforts and political interactions.

Environmental groups also understand the threat posed by abandoned underground storage tanks, and are concerned that all of these tanks may not be located or investigated. They are concerned that local and state regulations may also be inadequate but may still be accepted by the federal government due to bureaucratic and political reasons.

They are also concerned over the scientific and technological limitations for detecting and evaluating the threat posed by leaked products. This basic lack of information may result in inadequate limitations for final cleanup of contamination incidents. They are further concerned that this lack of adequate scientific knowledge, combined with the finalization of underground storage tank regulations, will not provide the needed safeguards to protect environmentally sensitive areas which may be affected by leaking underground storage tank contamination

E. Government Agencies

Government agencies are faced with a multitude of problems when both dealing with leaking underground storage tanks and the development of timely and effective underground storage tank programs. These problems can be categorized as: (1) unclear jurisdictions, (2) "Who is responsible for cleanup?" (3) "What is an adequate underground storage tank program?" (4) "How clean is clean?" and (5) general institutional concerns.

1. Unclear Jurisdictions

The effects of leaking underground storage tanks and petroleum product contamination are complex and highly variable. Environmental pollution, toxic and carcinogenic chemical health threats, and fire and explosion damage are often direct dangers from petroleum product pollution from leaking underground storage tanks. Product loss,

from a governmental view, also includes the loss of tax revenues and possible loss of controlled product quality. State and local governments are often not organized in a fashion which grants the jurisdictional responsibility for these effects to any single agency. Yet, all of these problems must be addressed during leaking underground storage tank incidents and the development of underground storage tank programs. Which state or local agency should receive jurisdiction for an underground storage tank program, and which can organize and handle all of these various problems?

State governments will be given the lead in underground storage tank programs in most states, with local ordinances given priority if considered more or equally stringent. Within state government, however, the organizational structure may not be conducive to easily determining underground storage tank jurisdiction. States with single environmental or natural resource departments can fairly easily endow these organizations with the responsibility. Other states which are not so organized may struggle with the determination. Political power plays and in-fighting for related underground storage tank funds and responsibility could result, especially in economically-strained states. Response by the government agencies to leaking underground storage tank incidents and dangers may be delayed because the incidents must be carefully examined to determine whether the current threat falls under local, state, or federal jurisdiction.

2. Who is Responsible for Cleanup

When a leaking underground storage tank incident becomes evident, the source or the responsible party cannot always be located. Who is then capable of evaluating the extent of the contamination, abating the effects, and cleaning up the contamination? The evaluation and cleanup of leaking underground storage tank incidents is a very costly and time-consuming task.

State and local governments are not always equipped, trained, or financially capable of properly accomplishing cleanup, or paying to have it done. Yet the incidents exist and their associated dangers and threats to property and human health can become increasingly evident and widespread. Unless the state or local governments have set up a tax or fee-based response fund, the agencies and departments, with their various responsibilities, must abate the threats as they become evident without ever effecting a cure for the incident.

3. What is an Adequate Underground Storage Tank Program?

With the increasing threats posed by leaking underground storage tanks, federal, state, and local governments are rushing to develop underground storage tank programs to control the problem and related costs of handling leaking underground storage tank incidents. Unfortunately, the complexities involved with causes and cures for underground storage tank problems often exceed even the scientific community's understanding, as well as the government's understanding. How, then, can adequate programs be developed, and who decides what is adequate and what is not?

The current philosophy appears to be that of watching programs which have been developed by state and local governments which have been hardest hit by leaking underground storage tank incidents. If these programs prove themselves in time, certain components of the programs are incorporated into the programs being developed by other government agencies. These adopted components must, however, be deemed reasonable, functional, and politically proper by the political climate within each government. Whether this philosophy works must be tested in time along with the already developed underground storage tank programs.

The problem, however, still exists. What is an adequate underground storage tank program? Are the existing programs over-regulating underground storage tank systems? Are they underregulated? The results of an inadequate program can have dramatic effects on the entire business community as well as the local environments.

4. How Clean is Clean?

When a leaking underground storage tank incident occurs and cleanup of the contamination is initiated, when does the cleanup stop? How clean is clean? This is a continuing question for any pollution remediation undertaking.

Unfortunately, with the increasing incidents of leaking underground storage tanks, the question arises more frequently, and its answer can affect nearly every community which has service stations or other types of underground tanks.

The scientific understanding of the interactions of the components of petroleum products in the subsurface is unclear. The toxicity and other health impacts of the products are not fully researched. The ability to detect the various components at potentially health threatening levels is limited and often still in the developmental stage. At what point will the natural environment be capable of handling residual contamination so that man-initiated clean-up can stop? These fundamental details must be addressed before a realistic answer can be determined for the question "How clean is clean?"

Meanwhile, leaking underground storage tank contamination incidents are being cleaned up with no real guidelines for when remediation is complete. The costs of continued cleanup, monitoring residual contamination, and unexpected health impacts are expensive and rising. The burden of the expense is absorbed by the business community, as well as, local, state, and the federal governments. Are the cleanup requirements excessive? Are they not enough?

5. General Institutional Concerns

The principal criteria for selecting remediation procedures should be the water quality level to which an aquifer should be restored, and the most economical technology available to reach that quality level. Unfortunately, there are numerous institutional limitations that sometimes override these criteria in determining if, when, what, and how remediation will be selected and carried out (Wilson et al., 1986).

Responding to a ground water contamination problem is likely to require compliance with several local, state and federal pollution control laws and regulations. If the response involves handling hazardous wastes, discharging substances into the air or surface waters, or the underground injection of wastes, federal pollution laws apply. These laws do not exempt the activities of federal, state, or local officials or other parties attempting to remediate contamination events. They apply to generators and responding parties alike, and it is not unusual for these pollution control laws to conflict. For example, a hazardous waste remediation project may be slowed, altered or abandoned by the imposition, upon the party undertaking the effort, of elaborate RCRA permit requirements governing the transport and disposal of hazardous wastes.

In situ remediation procedures may be subject to permitting or other requirements of federal or state underground injection control programs. Withdrawal and treatment approaches may be subject to regulation under federal or state air pollution control programs or to pretreatment requirements if contaminated ground water will be discharged to a municipal wastewater treatment system. Also, pumping from an aquifer may involve a state's ground water regulations or well construction standards and well spacing requirements as well as interfere with various competing legal rights to pump ground water.

IV. Research Needs for Optimized Remedial Techniques

Ground water pollution from leaking underground storage tanks represents an issue of recent major attention from a national perspective. Treatment of contaminated subsurface environments, particularly through the use of in situ biorestoration, has an even shorter history. Accordingly, as this remediation technology develops, many technical research needs can be identified. Examples of these needs will be discussed in terms of evaluating the effectiveness of physical containment techniques, enhancing vadose (unsaturated) zone pollutant removal techniques, and enhancing microbial population densities.

A. Evaluation of Effectiveness of Physical Containment Techniques

Physical containment measures include hydraulic barriers, vertical impermeable barriers, such as slurry walls and grout curtains, and subsurface drains and interceptor trenches. While these measures may be effective in terms of containing or excluding ground water flow, there are unresolved questions relative to the retention of certain solutes, both initially and over time. Examples of research questions which need to be answered include:

(1) What is the effectiveness of hydraulic barriers in non-homogeneous subsurface environments?

(2) What is the rate of increase in the permeability of bentonite slurry walls in the presence of certain organics?

(3) What design approaches can be used to optimize the usage of physical containment techniques (minimize the costs) in conjunction with pumping, pumping and treating, and/or in situ treatment remediation measures?

B. Enhanced Vadose Zone Pollutant Removal Techniques

Products released from leaking underground storage tanks can be retained in the vadose zone as a result of both physical and abiotic processes. Decomposition products may also be retained as a result of biotic degradation and subsequent abiotic processes. In this context, the vadose zone can be viewed as a "reservoir" which slowly releases contaminants to the saturated zone over time. Therefore, remediation techniques which would enhance the removal and/or transport of contaminants from the vadose zone would be desirable. Examples of research questions which need to be answered include:

(1) What chemical measures can be used to mobilize contaminants held in the vadose zone as a result of adsorption, ion exchange, precipitation, and/or complexation?

(2) Can man-induced changes in subsurface environmental conditions, such as changes in pH and oxidation-reduction potential, be used to mobilize contaminants?

(3) Can microbial degradation processes in the vadose zone be optimized through the controlled addition of nutrients, enzymes, and bacterial seed organisms?

(4) What design approaches and/or laboratory tests can be used to optimize man-controlled hydraulic flushing of vadose zone pollutants, both with and without recycling of extracted ground water from the polluted area?

C. Enhancement of Microbial Populations

The current literature indicates that in situ biorestoration is dependent upon the indigenous microflora; bacterial seed organisms are often added in biorestoration treatment schemes but their role in pollutant degradation is yet undemonstrated. Usually, stimulation of the native microflora results in increases in bacterial populations in the active biorestoration zone. The increases should coincide with bacterial degradation and may be limited by the availability of nutrients, lack of optimum environmental conditions for degradation, and/or lack of microorganisms adapted to the decomposition of leaked organic products. Therefore, increasing microbial population densities may be necessary in order to optimize the environmental conditions for in situ biorestoration. Examples of research questions which need to be answered include:

(1) What are the optimum nutrient concentrations for achieving in situ biorestoration of different classes of organic compounds?

(2) What are the optimum environmental conditions (pH, oxidation-reduction potential, micronutrients, etc.) necessary to achieve in situ biorestoration of different classes of organic compounds?

(3) Can laboratory development of acclimated microorganisms enhance in situ biorestoration, and what laboratory tests/procedures are necessary to achieve this acclimation?

(4) What design approaches and/or laboratory tests can be used to optimize microbial population densities for in situ biorestoration?

(5) What are the best methods for achieving in situ mixing of the bacterial populations, nutrients and micronutrients, and organics?

(6) What are the optimum (most cost-effective) combinations of in situ biorestoration and interdiction wells and surface treatment to achieve ground water remediation?

(7) Can we predict clean-up efficiencies using mathematical models that incorporate rate coefficients for target pollutants that are determined in site-specific aquifer materials?

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85

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