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Cleanup of Releases from Petroleum USTs:
Selected Technologies

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Preface

Cleaning up a gasoline release from an underground storage tank (UST) normally requires short-term emergency measures as well as long-term corrective actions. Short-term emergency measures are the immediate steps taken to abate imminent safety and health hazards. This handbook focuses on long-term remediation and site restorations. It has been assumed that emergency measures have already been taken to remove any immediate explosion or health threat and that the task at hand is to clean up the gasoline that has leaked from the tank and moved into the environment.

The objective of this handbook is to provide engineering-related information on costs, efficiencies, and limitations of corrective action technologies aimed at removing petroleum-related contaminants (principally associated with gasoline) from the subsurface. While many technologies exist for the cleaning of soil, air, and water, only a limited number possess demonstrated performance records and have progressed to full-scale applications. This handbook concentrates on those technologies that have been widely applied.

This is not a design manual and should not be used as such. Sufficient detail on corrective action technologies is provided so that state and local government personnel can adequately evaluate corrective action methods and plans proposed by responsible parties and their consultants. Although this report will help everyone in understanding the basics of corrective action technologies, some of the information may be more helpful if the reader has training or experience in chemistry or engineering.

To compare and contrast the various corrective action techniques, each proven technology is evaluated on the basis of several important criteria:

Effectiveness. How effective is the technology in removing contaminants?

Cost. What are the capital and operation and maintenance (O&M) costs of the technologies? What are the projected service lives? How does cost vary with time and removal efficiency? (Costs are reported in this document in 1986 dollars.)

Reliability. How consistently can the technologies remove the contaminants of concern and over how long a period of time?

Ease of Operation. How complex is the technology? Are specially trained personnel required for O&M activities?

Limitations. What factors might reduce the effectiveness or reliability of a technology or limit its applicability in a given situation?

Contents

Figures

Tables

Acknowledgments

Cleanup of Releases From Petroleum USTs: Selected Technologies

Summary of Findings

Only a limited number of technologies to clean soil, air, and water of the contaminants principally associated with gasoline are available that (a) have demonstrated performance records and (b) have progressed to full-scale application. This Summary reviews these technologies in terms of their removal efficiencies, limitations, and costs.

Recovery of Free Product From Water Table

The two technologies most commonly used to limit the migration of floating gasoline across the water table are the trench method and the pumping well method. A variety of equipment can be used to recover the free product. Typically, skimmers, filter separators, and oil/water separators are used in trench recovery, and single- and dual-pump systems are used with the pumping wells.

Containment of Free Product

The trench method is most effective when the water table is no deeper than 10 to 15 ft below the ground surface. Excavation of the trench is easy to undertake, and with this method the entire leading edge of the gasoline plume can be captured. However, the trench method does not reverse groundwater flow, so it may not be appropriate when a potable well supply is immediately threatened. Cost: about $100/yd^3 of soil excavated.

A pumping well system is normally used for deep spills, when water table depth exceeds 20 ft below the ground surface. The direction of groundwater flow can be reversed with this system. Cost: $100 to $200/ft for 4-in to 10-in gravel-packed galvanized steel wells. This cost includes engineering and labor.

Recovery Equipment

Skimmers, filter separators, surface-mounted product recovery pumps, aboveground oil/water separators, and dual pump systems can all be used to separate gasoline from groundwaters. Dual pump systems and oil/water separators are typically used for deeper releases. Skimmers can achieve up to 99 percent recovery of all hydrocar-

bons floating on the water surface. Cost: $6,000 to $7,000; the addition of a water table depression pump to expedite gasoline flow can increase capital cost of skimming system to $12,000 to $13,000 (approximately doubles the cost). Filter separators can reduce spill thickness to a sheen. For additional recovery, the top layer of the gasoline-water mixture must be removed from the well and treated aboveground. Filter separators can only be used to recover spills 20 ft or less below ground surface, and only with surface-mounted pumps. (Submersible pumps would cause the floating separator to sink.) Cost: $6,000 to $7,000; the addition of a water table depression pump to increase gasoline flow can increase capital costs of separation system to $12,000 to $13,000 (about double).

Aboveground oil/water separators are large tanks into which the recovered gasoline-water mixture is pumped and allowed to separate. Tanks range in size from 1,000-gal units to 10,000-gal units. To achieve the necessary retention time, separators must be sized at least 10 times larger than the groundwater extraction rate. Cost: $6,000 (1,000 gal) to $16,000 (10,000 gal).

Dual pump systems can remove up to 99 percent of free floating product. The most commonly used gasoline/water separation units, these systems consist of a water table depression pump and a product recovery pump. The depression pump creates cones of influence that allow gasoline to accumulate; the product recovery pump, which is equipped with gasoline sensors, brings only the gasoline to the ground surface. Cost: $12,000 to $14,000 for the two types of pumps. Because at least two pumps are required, operation and maintenance (O&M) costs are higher than with other methods.

Case Studies

Case studies of groundwater contamination have led to three conclusions:

- Cost of recovering free product at a site depends more on the recovery method and equipment required for the cleanup than on the size of the spill.
- More than one gasoline-recovery option may be feasible at a given spill.
- Costs of free product recovery are small com-

pared to the cost of restoring hydrocarbon-contaminated groundwater to drinking water standards.

The case studies reviewed involved spills from 2, 000 gal to 100, 000 gal. Costs of recovery ranged from $43, 000 to $225, 000 (including equipment, labor, engineering, and hydrogeologic services). On average, only 29 percent of the spilled product was recovered, at a cost range of $2 to $93 per gallon.

Removal of Gasoline From Unsaturated Soils

Soil treatment is an essential component of a corrective action plan. After a spill, hydrocarbons in the unsaturated zone can eventually enter the groundwater, if the soil is not treated. A number of techniques are used, but they vary in cost and effectiveness. Excavation and disposal is the most widely used corrective action for contaminated soil. Other methods include enhanced volatilization, incineration, venting, soil washing/extraction, and microbial degradation.

Excavation and Disposal

The most widely used corrective action, excavation and disposal, can be 100 percent effective. Moreover, soil excavation as an adjunct to removal of underground storage tanks (USTs) may help to eliminate the major source of continuing gasoline migration to the subsurface. The following limitations must be kept in mind:

- Standard backhoes (0.5 yd^3 capacity) can reach only a maximum depth of 16 ft. Larger backhoes (3.5 yd^3 capacity) are available that can remove soils at depths of up to 45 ft.

- Excavation is difficult in heavily congested areas or in areas close to or under buildings.

- The more soil brought to the surface, the greater the risk of exposure.

- Although tipping fees at some landfills are a reasonable $12/yd^3, disposal can cost up to $160/yd^3 if the soil is considered hazardous.

- The lack of uniform guidelines among the states for the disposal of contaminated soils means that transport risks may run high, as soil is sent from states with strict guidelines to the more permissive states.

Cost: $200 to $300/yd^3, which is relatively expensive. The result is that only small quantities of contaminated soil, say, 500 yd^3, are normally excavated and disposed. The trend is toward applying alternatives to land disposal, such as incineration or biodegradation, by which contaminants are destroyed.

Disposal of contaminated soils in batch asphalt plants is a practice not yet reported in the literature, but may be more common than most people realize. Some plants charge $55/yd^3 for accepting gasoline-contaminated soils; other plants refuse such soils because they must then observe the state laws governing hazardous waste treatment facilities.

Enhanced Volatilization

Theoretically, up to 99.99 percent of volatile organic compounds (VOCs) can be removed by enhanced volatilization, but this soil treatment method has not been widely applied in the field. Different methods of enhancing volatilization include rototilling, mechanical aeration, pneumatic conveyor systems, and low-temperature thermal stripping. Only thermal stripping has been documented to successfully remove contaminants with vapor pressures comparable to those of gasoline constituents. Limitations to enhanced volatilization include soil characteristics that constrain the movement of gasoline vapors from the soil to the air; contaminant concentrations that may create an explosion hazard; and the need to control dust and organic vapor emissions. Cost: $245 to 320/yd^3 soil treated; most effective with 15,000 to 18,000 tons of soil.

Incineration

By complete oxidation, incineration can eliminate 99.99 percent (or more) of gasoline constituents in soil. This technology is widely practiced and highly reliable. The associated limitations are that the soil must be brought to the surface, which increases the risk of exposure; incineration is usually appropriate only when toxics other than volatiles are present; and the permitting requirements may cause time delays. Cost: $200 to $640/yd^3 of soil. Soil volumes of less than 20,000 yd^3 will increase costs considerably.

Venting

Venting allows for the removal of gasoline vapors from unsaturated soils without excavation. It has been demonstrated to be effective in recovering as much as 99 percent of gasoline components in unsaturated soil. The technology has not been widely applied in the field, however, partly because critical design parameters remain undefined. Moreover, its effectiveness is uncertain because soil characteristics may impede free movement of vapors, create an explosion hazard, or cause high levels of organic emissions. Venting is relatively easy to implement and causes minimal disturbances to structures or pavement. Cost: $15 to $20/yd^3, which is inexpensive. It would become even more cost-effective when soil volumes exceed 500 yd^3.

Soil Washing/Extraction

With this approach, contaminants are leached from the soil and into a leaching medium, after which the extracted contaminants are removed by conventional methods. Removal of 99 percent of volatile organic compounds is possible under ideal conditions, but typical removal rates are less. High percentages of silt and clay in the soil may impede the separation of the solid and liquid after the washing phase. Since the process requires physical separation techniques (e.g., distillation, centrifugation, and evaporation), pilot studies are recommended before final design and implementation. Cost: $150 to $200/yd^3 of contaminated soil.

Microbial Degradation

Theoretically, gasoline removal efficiencies of 99 percent or more can be achieved with microbial degradation of contaminants. The technique has not been widely applied in the field, and additional research is required to confirm cost and effectiveness. The advantages of this technique are that the soil is usually treated in situ and the volatiles are completely destroyed. Gasolines composed principally of alkenes in the C^5 to C^{10} range would be the quickest to degrade. For its effectiveness, the technique is dependent on oxygen levels, nutrient levels, temperature, and moisture content of the soil. Cost: $66 to $123/yd^3. The combination of soil venting and microbial degradation is often one of the least costly and most effective corrective actions for treating gasoline-contaminated soils.

Current Soil Treatment Procedures

Much confusion exists about the hazard posed by gasoline-contaminated soil and how the soil should be treated. An informal survey of several states revealed that none require soil testing during UST excavations. Many states do require a fire marshal to be present to determine explosion hazards at sites where visual inspection shows soil to be contaminated. Landfill is the principal mode of disposal of contaminated soils, and time delays are common. None of the states surveyed have regulations preventing open aeration of contaminated soils to reduce the volatile organic compounds. Many excavators admit placing gasoline-contaminated soils on plastic sheets until the volatiles disperse so that the soil can be trucked to the local landfill.

Removing Gasoline Dissolved in Groundwater

The two most widely used technologies (employed in more than 95 percent of all cases) for removing that portion of the gasoline plume dissolved in groundwater are air stripping and filtration through granular activated carbon (GAC). Biorestoration is a cost-effective and promising alternative, but it has not been widely applied in the field.

Air Stripping Towers

For most volatile organics found in gasoline, packed towers have maximum removal efficiencies of 99 to 99.5 percent. Through air stripping, effluent concentrations of 5-µ/L volatile organics can be achieved. Concentrations less than 5 µ/L are not usually achievable because the technology is constrained by the size of the tower that would be required to achieve such a high removal efficiency. Critical design parameters include the type of packing material used, the air-to-water ratio, the stripping factor, and the tower height. Plastic packings are the most widely used; they are inexpensive and lightweight. Air-to-water ratios from 20:1 to 100:1 are common for aromatics removal in general and for those in gasoline in particular. Stripping factors between 3:1 and 5:1 are best suited for gasoline-related constituents. In designing a packed air tower, the following considerations are important:

- Zoning laws may restrict the maximum height of a tower.
- The tower, blower, and pumps may have to be enclosed, not only for noise reduction but also for aesthetic reasons.
- Influent air must be free of VOCs, so air intake must be situated to avoid "short circuiting" between the influent air and the tower effluent air.
- Gaseous demisters may be needed to prevent water from leaving the top of the tower.
- Vapor-phase treatment, if required, will double the cost of the packed air tower.

Because more contaminant can be adsorbed in an air-to-carbon loading than in a water-to-carbon loading, vapor-phase treatment with GAC may be advantageous. Cost: $50,000 to $100,000 (including labor, engineering, and contingencies), which is 50 to 80 percent less than comparable costs to treat with GAC. On a volume-treated basis, typical costs at a leaking UST site are $5 to $25 per thousand gallons.

Granular Activated Carbon Adsorption

GAC adsorption can remove as much as 99.99 percent of the organic compounds found in gasoline. To achieve effluent concentrations of 5 µ/L or less for gasoline constituents, GAC is almost always required. Designing a GAC system is complex, as the following points illustrate:

- Each contaminant competes for carbon pore space.

- The EBCT (empty bed contact time) is directly related to the size of contactor needed; 15 minutes is the usual minimum contact time for gasoline spills.

- Fixed bed columns and pressure filters are normally used in cleaning leaking UST sites; use of pressure filters saves repumping costs because they allow higher surface loading rates and pressure discharge to the distribution system.

- The ability of a compound to be removed with GAC is a function of its solubility. Low-solubility compounds adsorb better than high-solubility compounds. The order in which gasoline components break through (from earliest to latest) is: benzene, ethylbenzene, toluene, xylene, naphthalene, and phenol.

- Some compounds found only in certain gasolines might break through earlier than benzene because of their low adsorption capacities: methyl-tertiary butyl ether (MTBE), ethylene dibromide (EDB), and ethylene dichloride (EDC). Less than 40 percent of today's gasolines contain EDB or EDC. Only 10 percent contain MTBE. It is more expensive to design for the removal of these compounds than it is to design for benzene removal.

- Effectiveness of system may be reduced by excessive iron or manganese, and hardness of the water. If iron concentration exceeds 5 mg/L, removal prior to carbon filtration is recommended.

- Spent carbon from leaking UST sites is usually landfilled. Caution must be exercised in handling gasoline-saturated carbon tanks because they can self-ignite.

- GAC is most effective when used with air stripping. Carbon life can be extended by treating gasoline-contaminated groundwater with packed air towers. A two-phase approach is best. The first phase is to install a packed air tower. Its performance would then be monitored to determine effluent concentrations, and the need for a second-phase treatment with GAC.

Cost: $300,000 to $400,000 for a typical GAC unit. Costs include labor, engineering, and contingencies. O&M costs range from $25,000 to $30,000/yr.

Biorestoration

Under proper conditions, trace concentrations of aromatic hydrocarbons can be reduced by 99 percent with this technique. Its distinct advantage is that the gasoline contaminants are completely destroyed, not merely transferred to another environmental medium. Its applicability depends on dissolved oxygen concentrations, available nutrients, temperature, pH, salinity, concentrations of contaminants, presence of predators, and water content. Through biorestoration, effluent concentrations

in the ppm-range (mg/L) can probably be attained; treatment to ppb-levels (µg/L) requires manipulation of the system (encouragement of co-metabolism or degradation by an added substrate). Currently, the technology appears to work best as a "polishing" step. Cost: few data exist, but costs range from $30 to $40/yd^3 treated to $10,000/acre treated, and from $4 to $6/lb of contaminant removed.

Point-of-Entry Treatment and Extension of Water Distribution Systems

Restoration of the polluted aquifer can often take months or years, during which time users of the water must find alternative water sources. Two alternatives are point-of-entry treatment systems and extension of the water distribution system.

Point-of-Entry Treatment

Systems which treat water at the point of entry into a home are preferable to point-of-use systems that can be placed on individual taps. Research indicates that showering in water that contains volatile gasoline compounds may pose a serious health threat; therefore, only point-of-entry systems are considered appropriate at homes with gasoline-contaminated well water. There are several types of devices: reverse osmosis, ion exchange, distillation, aeration, and carbon adsorption. Carbon adsorption is the most effective in eliminating dissolved gasoline compounds. Carbon adsorption is capable of removing more than 99 percent of dissolved gasoline compounds, including benzene, toluene, and xylene.

Activated carbon can adsorb dissolved compounds for water, but only up to a point. To eliminate the risk of contaminant breakthrough, two carbon tanks in series are installed, and the effluent water is tested periodically for the presence of VOCs. The most serious limitation associated with carbon adsorption point-of-entry treatment systems is that significant changes in contaminant concentrations may go undetected. If the influent concentrations fluctuate and exceed the design capacity of the system, contaminant breakthrough could occur without the resident knowing it. For this reason, it is recommended only as an interim remedial measure in a home. Cost: Carbon tanks, from $700 to $900; carbon replacement and disposal, from $100 to $200 per replacement; testing for VOCs, $250. Additional water quality improvement equipment, such as chemical feed units, softeners, filter, retention tanks, and polishers, are in the $500 to $950 range for each piece of equipment. Case studies reported in this manual indicate that annual capital and O&M costs are from $4,000 to $5,000 per household.

Extending Water Distribution System

Cost is usually the primary consideration in extending water mains to homes affected by a contaminated well field. This measure is often the appropriate long-term solution. Cost: transmission mains (for long distances) range from $27/linear foot (lf) for 6-in mains to $40/lf for 12-in mains, and to $84/lf for 24-in mains. Distribution mains (for short distances between the transmission main and the individual home or building) range from $44/lf for 6-in mains, to $56/lf for 12-in mains, to $100/lf for 24-in mains.

Section 1
Introduction

Gasoline is a complex mixture of hydrocarbons comprised principally of alkane, alkene, and aromatic hydrocarbons. Gasoline spilled or leaked into soil volatilizes because of its high vapor pressure, filling pore spaces with vapors. Gasoline vapors, as well as gasoline in the liquid phase, are subject to further dispersal and migration as precipitation moves into and through the subsurface. Gasoline in either state can dissolve in water and eventually move into groundwater supplies. It is important, therefore, that gasoline in unsaturated soils, as well as free product and that dissolved in groundwater, be removed to minimize further dispersal of the contaminants.

Cleaning up a release from an underground storage tank (UST) requires both short-term emergency measures and long-term corrective actions. Short-term emergency measures involve taking immediate steps to abate imminent safety and health hazards, including potential explosions. These emergency steps include notifying appropriate government officials, stopping the release, and removing hazardous substances as necessary to prevent further releases and to allow inspection and repair of the tank system.

The focus of this handbook is on long-term remediation and site restoration that occurs after emergency measures have already been taken to remove any immediate explosion or health threat. The task at hand is to clean up the released gasoline that has moved into the environment and is adsorbed to soil particles, floating as free product on the water table, or dissolved in groundwater. In cleaning up a site, it is essential that corrective actions be designed to address the released contaminants in each and every medium in which they are found. Cleaning up contaminated groundwater without cleaning up contaminated soil could result in continued contamination as rainfall percolates through the soil. Cross-media contamination issues also must be addressed in developing a corrective action plan for a particular site, for example, vapor emissions from air stripping towers and soil venting systems.

A variety of corrective actions can be used at a

leaking UST site to treat contaminated soil, recover free product, treat vapors generated by evaporating aromatics, and remove contaminants dissolved in groundwater. They differ in their cost, removal efficiencies, reliability, and applicability.

Objective of This Handbook

The objective of this handbook is to provide engineering-related information regarding the removal efficiencies, limitations, and costs of alternative corrective action technologies for removing contaminants (principally associated with gasoline) from the subsurface. While a large number of technologies exist to clean soil, air, and water, only a limited number possess demonstrated performance records and have progressed to full-scale applications. This handbook focuses on those corrective action technologies that have been widely proven to be effective and reliable, or that are promising but lack full-scale application and review.

Ultimately this handbook can serve as a reference document for local and state personnel who must evaluate and make decisions about the most appropriate corrective actions to use at a particular site. The cost curves, design equations, and related implementation issues will assist them in making informed and effective decisions. The corrective action field is changing, but the information presented here will still help direct attention to the main elements and factors in conducting cleanups.

The overall intent of this handbook is to provide personnel involved with corrective actions at UST sites with a summary of the principal components, design considerations, and costs behind the technologies, and to identify conditions and situations where one corrective action might be preferred over another.

This is not a design manual and should not be used as such. Each situation is unique. A professional engineer or similarly qualified individual should be sought to design and install any equipment described in this report.

To compare and contrast the various corrective action techniques, each proven technology is

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evaluated on the basis of several important criteria:

- Effectiveness. How effective is the technology in removing contaminants?

- Cost. What are the capital and operation and maintenance (O&M) costs of the technologies? What are the projected service lives? How does cost vary with time and removal efficiency? (Costs are reported in this document in 1986 dollars.)

- Reliability. How consistently can the technologies remove the contaminants of concern and over how long a period of time?

- Ease of Operation. How complex is the technology? Are specially trained personnel required for O&M activities?

- Limitations. What factors might reduce the effectiveness or reliability of a technology or limit its applicability in a given situation?

Limitations of This Handbook

This handbook necessarily focuses on widely applied and proven technologies, ones that could be recommended at a site to secure desired results. The technologies are described with specific attention focused on removing gasoline from the subsurface, especially the major constituents of concern in gasoline: benzene, toluene, and xylene (BTX).

There are a number of regulatory issues associated with the implementation of corrective action technologies, particularly with soil treatment technologies. The regulatory issues include securing the appropriate permits, establishing standards for cleanup, determining when contaminated soil is "hazardous," and ultimate disposal of recovered free product, contaminated soil, and groundwater. This handbook does not cover these issues, except for those touched upon under the "Limitations" section for each technology. Rather, the focus of this study is on engineering-related considerations for each technology.

Other points to keep in mind when reading this handbook are:

- Composition of Gasoline

    This handbook focuses on corrective actions for cleaning up the principal constituents of concern in gasoline for which reliable data exist. Reliable data on the toxicity, chemical characteristics, and weight for most of the approximately 240 compounds which have been identified in gasoline do not exist for every constituent. Consideration

must be given to the "minor" constituents as well. In addition, there are a number of proprietary additives for which little or no data exist.

- Site-Specific Conditions

    The optimal design and performance of all technologies is highly dependent upon site-specific conditions. To optimize system performance, field and pilot testing at individual sites should be undertaken prior to full implementation. The generalized analyses in this report are based on "typical contamination incidents" and the typical concentrations one is likely to encounter in a leak situation.

- Soil Treatment Technologies

    Soil treatment has not received widespread application. Much research has been gathered on various soil treatment techniques, but a great deal of uncertainty remains about how the techniques work, and what the controlling factors are to achieve maximum effectiveness. Although the theories and equations are not as thoroughly developed as they are for other technologies, such as air stripping and carbon adsorption, soil treatment techologies are not less useful nor less important. Soil contamination must always be addressed, and some kind of soil cleanup is usually necessary.

Other Studies

Several reports would serve as useful companion documents to this one:

- Camp Dresser & McKee Inc. 1986. Interim Report - Fate and Transport of Substances Leaking From Underground Storage Tanks.

    Describes in detail the various compounds that make up gasoline and how they move in and through the environment.

- PEI. 1987. Underground Storage Tank Corrective Action Technologies. Prepared by US EPA, Hazardous Waste Engineering Laboratory, Cincinnati, Ohio.

    Provides detailed information on the "universe" of technologies that are available to remove gasoline from the subsurface. The report is a comprehensive examination of what is available (compared to the few technologies that are typically used).

- Radian Corporation. 1987. Air Strippers' Air Emissions and Control (Draft).

    Provides information on vapor-phase discharges from air stripping towers, including cost data.

Organization of This Handbook

The principal corrective actions for UST releases are discussed in detail separately in the sections that follow. Section 2 introduces the chemicals of concern and describes how they move through the environment. Section 3 describes various methods aimed at recovering free product from the water table. Section 4 describes soil treatment techniques, and Section 5 addresses the removal of contaminants dissolved in groundwater. Because Section 5 addresses the treatment of constituents dissolved in groundwater, an area about which much information exists, it is printed on colored paper to set it apart as the section of this report that contains the most extensive engineering information. As such, it will likely be the most useful section to a reader reviewing corrective action plans. Section 6 provides information on alternative water supplies such as point-of-entry systems and water distribution system extension, possible shorter term solutions while the longer term corrective actions are being implemented. Section 7 is a summary of findings, and Section 8 is an index of key words.

Section 2

Fate and Transport of
Gasoline in the Subsurface

To implement corrective actions effectively, it is essential to understand how gasoline behaves in the subsurface. Fate and transport mechanisms are complex. The behavior of chemicals in the subsurface is governed not only by their physical and chemical properties but also by the characteristics of the soil and rock formations through which the chemicals move.

Chemicals can exist in the subsurface in four general states: as free product (pure compound);

adsorbed to soil; as vapor; or as solutes in water (see Figure 1). In conducting corrective action, the person responsible needs to address the removal of contaminants in each state. The following sections of this handbook pertain to the cleanup of one or more of these four chemical states. Recovery of free product is discussed in Section 3. Removal of chemicals adsorbed to soil is discussed in Section 4. Removal of contaminants dissolved in groundwater, as well as treatment of the vapor phase of the contaminant, is discussed in Section 5.
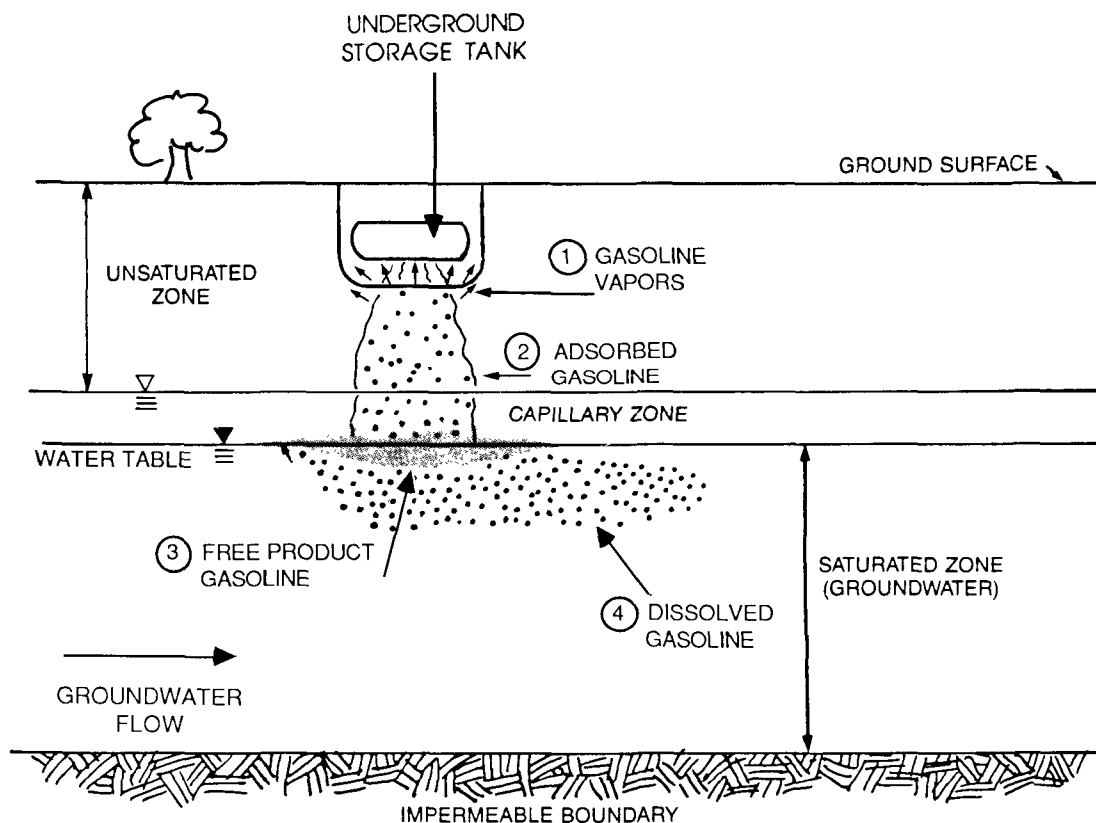
Figure 1.   Schematic of the subsurface environment and four phases of contamination.

The extent to which each phase of a chemical partitions and migrates in the subsurface is a function of several variables, including moisture content, bulk density and permeability of the soil and rock formations, air and gas vapor pressure within pore spaces, temperature, pH, and the presence of bacteria that decompose the contaminants. Analyzing the fate and transport of gasoline in the subsurface is a particularly complicated process because gasoline is a mixture of chemicals. Each compound used in commercial gasolines has a unique set of physical and chemical properties that determines its multiphase flow characteristics. Consequently, it is often difficult to predict how each gasoline component will behave and the extent to which it will migrate in soil and rock formations. A brief discussion follows that covers the current understanding of the fate and transport of gasoline and its components in the subsurface.

Factors Affecting Transport

Properties of the Gasoline

To understand how gasoline behaves in the subsurface, its relevant characteristics must be considered.

* Gasoline ranges in density from 0.72 to 0.78 g/cm^3 and is less viscous than water. (Viscosity is a measure of a liquid's resistance to flow; since gasoline is less viscous than water, it moves more easily through soil).

* Gasoline is immiscible in water (i.e., the fluids displace one another without mixing); however, there are many components of gasoline which readily dissolve upon contact with water.

* Some gasoline constituents are highly volatile.

* Some compounds are readily biodegraded in the presence of soil bacteria and oxygen.

Gasoline is a mixture of different compounds. A typical blend contains nearly 200 different hydrocarbons in addition to additives which serve as anti-knock agents, anti-oxidants and sweetening inhibitors, metal deactivators, corrosion inhibitors, deicing and anti-stall agents, preignition preventors, dyes, and upper cylinder lubricants. Each compound exhibits different physical and chemical properties which control its fate and transport in a soil system, and therefore, it is difficult to study the behavior of a specific gasoline as a whole.

Thirteen chemicals commonly found in gasoline (nine hydrocarbons and four additives) are regulated as hazardous substances under the Comprehensive Emergency Response, Compensation and Liability Act (CERCLA). This group includes benzene, toluene, and xylenes (BTX), and addi-

tives such as ethylene dibromide (EDB) and tetraethyl lead. These chemicals are listed in Table 1, along with values for their toxicity, water solubility, vapor pressure, and degree of biodegradability.

Although the physical and chemical properties shown in Table 1 are usually adequate for characterizing the behavior of gasoline under laboratory conditions, they may not be adequate for describing behavior in a subsurface environment.

Structure of the Subsurface

Soil particles and rock fragments are separated by voids called pore spaces. The pores are often interconnected, forming a network of fine channels through which water and air can circulate. Subsurface formations are characterized based on their pore structure and water-bearing capacity. Figure 1 depicts three distinct zones: the unsaturated zone, the capillary zone, and the saturated zone.

The Unsaturated Zone

The unsaturated zone (also referred to as the aeration zone or vadose zone) is the region between the ground surface and the top of the capillary zone. Water is retained there by adsorption on the surface of particles and by capillary forces (suction). Capillary forces are adhesive and cohesive forces which bind water molecules to solid surfaces.

The maximum volume of water that can be held in the pores by adsorption and capillary forces is referred to as the residual saturation of water. As defined by CONCAWE (1979), residual saturation is the minimum content a fluid must attain in order to move in a porous medium; or alternatively, the threshold content below which the fluid is no longer able to move. Unsaturated zone pore spaces that are not filled with water contain air that can circulate freely.

The Capillary Zone

The capillary zone is a transition region between the unsaturated zone and the saturated zone. Moisture content in the capillary zone ranges from residual saturation near the unsaturated zone to complete saturation at the water table. The capillary zone varies in thickness depending on the size of the soil particles and the diameter of the pore spaces. The finer the pores, the higher the capillary rise. The homogeneity of the subsurface formation also influences the thickness of the capillary zone. In homogeneous porous media, the zone thickness will tend to be constant, whereas in nonhomogeneous formations, the thickness can vary considerably.

Table 1

Physical and Chemical Properties of Toxic Gasoline Components

Compound	Mass		Prevalence	Fate and Transport			Toxicity	Confidence in Data[4]
	% Volume in Gasoline	% Weight[1] in Gasoline	% of Gasolines Containing Chemical	Water Solubility at 20°C (mg/L)	Vapor Pressure (torr)[2]	Degree of Biodegrad-ability	Final RQ (kg)[3]	
Benzene	1-2	0.81	>99	1,780	75.0	Some	4.54	+
Toluene	4.0	12.02	>99	515	22.0	Some	454.00	+
Xylene-M	5-8	3.83	>99	175	5.0	Some	454.00	+
Xylene-O	5-8	1.93	>99	162	6.0	Some	454.00	+
Xylene-P	5-8	1.58	>99	198	6.5	Some	454.00	+
Ethylbenzene	2-5	1.70	>99	152	7.0	Some	454.00	+
Naphthalene	0.7	0.10	>90	31.1	1.0	Readily	45.40	+
Phenol	-	-	>90	66,667	0.5	Readily	454.00	+
EDB	0.01	0.024	<40	4,310	11.0	Some	4.54	0
EDC	0.01	<0.024	<40	8,690	61.0	Some	45.40	0
Tetraethyl Lead	-	-	<40	0.08	0.2	Some	4.54	0
Dimethylamine	-	-	-	1×10^6	1,345.0	Readily	454.00	-
Cyclohexane	<0.7	0.17	-	66.5	77.0	Some	454.00	-

[1] Source: Maynard and Sanders, 1969.
[2] At 20°C.
[3] The lower the RQ value, the more toxic the chemical is in pure product form
[4] + = highly confident; 0 = somewhat confident; − = not confident.

The Saturated Zone

The saturated zone is the region below the unsaturated zone and the capillary zone where the pore spaces are completely saturated with water. In the saturated zone, the water pressure increases with depth. The boundary where the pressure in the water phase equals the atmospheric pressure is called the piezometric surface or water table. The area below the water table may be thought of as a reservoir, the capacity of which equals the total volume of the pore spaces filled with water.

Subsurface reservoirs, or aquifers, perform two important functions: they act as storage reservoirs and water-carrying bodies. Water-carrying capacity is a function of effective porosity (i.e., total volume of interconnected pore spaces) and permeability. Permeability is the measure of a soil's resistance to the flow of liquids and is dependent on the diameter of the pores and the shape and orientation of the soil and rock particles. Groundwater flow through an aquifer is influenced by gravitational forces, but the rate at which the groundwater moves can vary significantly. Depending on the permeability of the aquifer and the flow gradient, groundwater can move at a velocity of only a few meters per year to several meters per day.

Multiphase Movement of Gasoline

Because gasoline is comprised of some highly volatile and soluble hydrocarbon fractions, its movement in the subsurface occurs in more than one phase. Gasoline components can move as solutes in the water phase, free product in the admissible phase, and vapor in the air phase. Multiphase flow is further complicated because each subsurface formation has different characteristic properties which govern the transport of substances through it. In the following discussion, multiphase transport of gasoline components is described for the unsaturated zone, the capillary zone, and the saturated zone.

Transport in the Unsaturated Zone

The depth to which gasoline penetrates the subsurface is most dependent on the volume discharged. As gasoline moves into the soil, it begins to migrate both vertically and horizontally. The vertical component is due to gravity, while the horizontal component is due to capillarity (the adhesive forces between the gasoline and the soil and rock particles). Migration occurs by successive permeation of larger areas. In a highly permeable homogeneous formation, the migration is mainly downward. In a less permeable homogeneous formation, capillary forces will have greater influence and migration has a more significant horizontal component. As shown in Figure 2, migration through heterogeneous formations results in a widely varying shape of the infiltrating gasoline body.

Vertical penetration in the unsaturated zone can be impeded in three ways: (1) when the threshold of residual saturation is reached (occurs when the gasoline body is adsorbed to soil and rock particles and trapped in capillary spaces); (2) when an impermeable layer exists in the path of the gasoline (migration is lateral until residual saturation is reached or until it reaches a discharge point); or (3) when the gasoline reaches the water table.

LAND SURFACE

HIGHLY PERMEABLE
HOMOGENEOUS SOIL

LESS PERMEABLE
HOMOGENEOUS SOIL

STRATIFIED SOIL WITH
VARYING PERMEABILITY
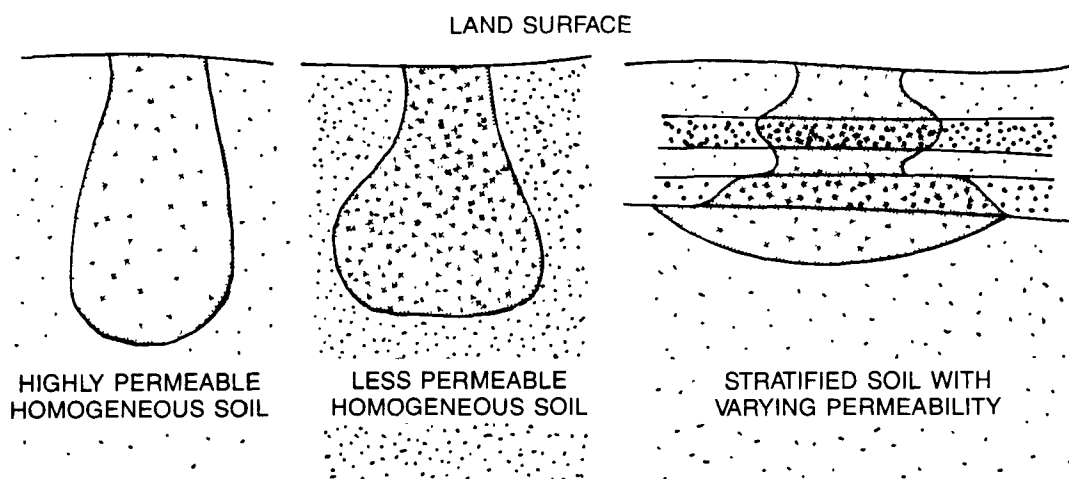
Figure 2. Contaminant transport through unsaturated homogenous and heterogenous soils.

The gasoline that remains in the unsaturated zone is partitioned among four phases: free product retained in pore spaces by capillary forces; solutes of gasoline components adsorbed onto particles; vapor in the soil air; and dissolved product in the soil water.

Retention by Capillary Forces

Capillary forces are attractive forces between gasoline and particles in pore spaces through which the gasoline moves. The dominant capillary force, adhesion (the attraction of liquid molecules for solid surfaces), holds gasoline molecules rigidly to soil and rock particles. These molecules in turn hold by cohesion (attraction of molecules to each other) other gasoline molecules which are further removed from the soil and rock particle surfaces. Together, adhesion and cohesion enable soil and rock particles to retain gasoline against the force of gravity. Capillary forces result in vertical and horizontal movement of liquids. The extent of capillary movement depends on pore size. In general, the finer the pore size, the greater the movement.

Adsorption Onto Particles

Sorption (the bonding of a solute to sorption sites on a solid surface) occurs through the following mechanisms: van der Waals forces, hydrophobic bonding, hydrogen bonding, charge transfer, ligand exchange, ion exchange, ion/dipole interactions, magnetic interactions, and chemisorption. The extent to which gasoline compounds adsorb to a specific soil or rock particle depends on the sorption potential of the chemicals; the organic carbon content of the particles; the texture, structure, and bulk density of the particles; clay and moisture content; cation exchange capacity; and pH.

Table 2 lists adsorption coefficients for specific gasoline compounds. The values presented are a measure of each compound's mobility potential based on its affinity for organic carbon. Of the toxic gasoline compounds listed, tetraethyl lead and naphthalene have relatively low mobility values and are likely to be adsorbed to the soil. Toluene, the xylenes, benzene, and phenol have high mobility values and, therefore, are more likely to appear in either the dissolved or gaseous phases.

Volatilization to Soil Air

Volatilization of gasoline compounds to the soil air depends on the potential volatility of the compounds and on soil and environmental conditions which modify the vapor pressure of the chemicals. Vapor pressure (the pressure exerted by a gas at equilibrium with respect to its liquid or solid phase) is directly proportional to volatility. Factors which influence vapor pressure and, consequently, volatility include soil parameters such as water content, clay content, and surface area, in addition to environmental factors such as temperature, wind speed, evaporation rate, and precipitation (Fleischer, 1987). Vapor pressure values for toxic gasoline components are listed in Table 1. The values range from 0.2 torr (760 torr = 1 atm) for tetraethyl lead to 75 torr for benzene.

For more information, see Vapor Transport in the Unsaturated Zone, p. 12.

Dissolution in Soil Water

Dissolution occurs as soluble gasoline compounds come in contact with water. The potential for dissolution of gasoline compounds to soil water is a function of each compound's solubility. Solubility is the

Table 2
Adsorption Coefficients for Gasoline Compounds

Chemical	K_{OC} Value
Tetraethyl Lead[1]	4,900 mL/g
(n) Heptane	2,361
(n) Hexane	1,097
Naphthalene[2]	976
(n) Pentane	568
Ethylbenzene[2]	565
Toluene[2]	339
1-Pentane	280
(o) Xylene[2]	255
Benzene[2]	50
Phenol[2]	50
Ethylene Dibromide	44

Source Lyman et al (1982).
[1] K_{OC} is a measure of the tendency for organic compounds to be adsorbed by soil. The higher the K_{OC} value for each compound, the lower the mobility and the higher the adsorption potential
[2] Also listed in Table 21 as a toxic compound.

partitioning of a chemical between the nonaqueous (gasoline) and dissolved phases. Not only does solubility determine the extent to which a contaminant will dissolve, it also affects other fate mechanisms. For example, a highly soluble substance often has a relatively low adsorption coefficient and also tends to be more readily degradable by microorganisms.

As shown in Table 1, several compounds are more soluble than benzene: phenol, EDC, EDB, and dimethylamine. Another constituent of gasoline known to be more soluble than benzene is methyl tertiary butyl ether referred to as MTBE, which is not shown on Table 1 because it is not considered toxic.

MTBE is being more widely used as an octane-enhancing additive to gasoline, especially because tetraethyl lead is being phased out. Although MTBE has been produced commercially only since 1979, it is now among the top 50 chemicals produced in the United States. Still, only about 10 percent of U.S. gasoline contains MTBE. The health effects of MTBE are generally poorly understood, especially at low levels. It has been classified variously as an irritant, as a possible central nervous system depressant, and formerly as having medicinal value (used to treat gallstones).

MTBE is extremely soluble in water: about 24 times more soluble than benzene (43,000 mg/L vs. 1,780 mg/L). Because of its high solubility, MTBE is easily transported by groundwater away from a spill site and will often have a larger plume than gasoline components such as benzene; the MTBE plume is thought to occur as a "halo" around the benzene plume. It has been detected at concentrations as high as 47 ppm, but is typically found at concentrations of 1 ppm or less (1 ppm = 1 mg/L). MTBE actually has a cosolvent effect, causing some of the other compounds in gasoline to solubilize at higher concentrations than they would normally in "clean" water.

Transport in the Capillary Zone

When free gasoline first reaches the capillary zone, its vertical migration is stopped. As more gasoline descends, a layer of increasing thickness forms and hydrostatic pressure is exerted, depressing the water table. As buoyant forces act to restore the original water level, lateral movement begins and a lens of gasoline forms and spreads out. Lateral spreading occurs in all directions, but the predominant movement is with the slope of the water table. Heterogeneities and permeability differences often influence the direction and extent of free gasoline migration in the capillary fringe. In heterogeneous soils, gasoline migration is along the path of least resistance. Soil permeability affects the rate and

thickness of lateral spreading. In low permeability soils, resistance to flow is high and a thicker lens will form; lenses formed in higher permeability soils are thin and fast-moving.

As in the unsaturated zone, transport in the capillary zone is governed by multiphase flow phenomena. However, the increased water content in the capillary zone affects the rates of volatilization and dissolution. As soil water content increases, volatilization and vapor transport generally decrease, and dissolution and solute transport generally increase. Free product migration occurs on top of the water table, but as the gasoline continues to spread, it is held by capillary forces in the soil matrix. When the free gasoline is exhausted, migration stops and residual saturation is reached.

Several technologies that are available to recover free product are discussed in detail in Section 3.

Transport in the Saturated Zone

Dissolved gasoline compounds reach the saturated zone in several ways:

● Infiltrating water passes through the gasoline bound in the unsaturated zone and leaches some compounds and carries them into the aquifer. These compounds then move with the groundwater gradient as a single phase.

● Free gasoline reaches the water table where some of the compounds dissolve and move with the groundwater gradient as a single phase (see Figure 3).

● Free product held in residual saturation in the unsaturated zone is submerged following a rise in the water table. Capillary forces binding the submerged free gasoline to the soil and rock particles resist buoyant forces pushing the gasoline up toward the elevation of the new water table. As a result, the gasoline remains in the saturated zone, and dissolution occurs freely (see Figure 4).

The movement of dissolved gasoline compounds in the saturated zone is governed by advection and dispersion. Advection is the movement of dissolved contaminants with the mean groundwater gradient. Dispersion describes how dissolved contaminants spread out and become diluted as they move. The effects of dispersion explain the observation that contaminants occupy more of the saturated zone than can be due to advection only.

Once gasoline components have dissolved in groundwater, removal becomes very costly. Typically, packed air towers and/or carbon adsorption are required for the removal of dissolved components of gasoline in groundwater. These groundwater treatment technologies are discussed in Section 5.

(A) CONTAMINANT IN DIRECT CONTACT WITH THE WATER TABLE

(B) GROUNDWATER CONTAMINATION RESULTING FROM SOLUTION OF CONTAMINANT IN PERCOLATING RECHARGE WATER
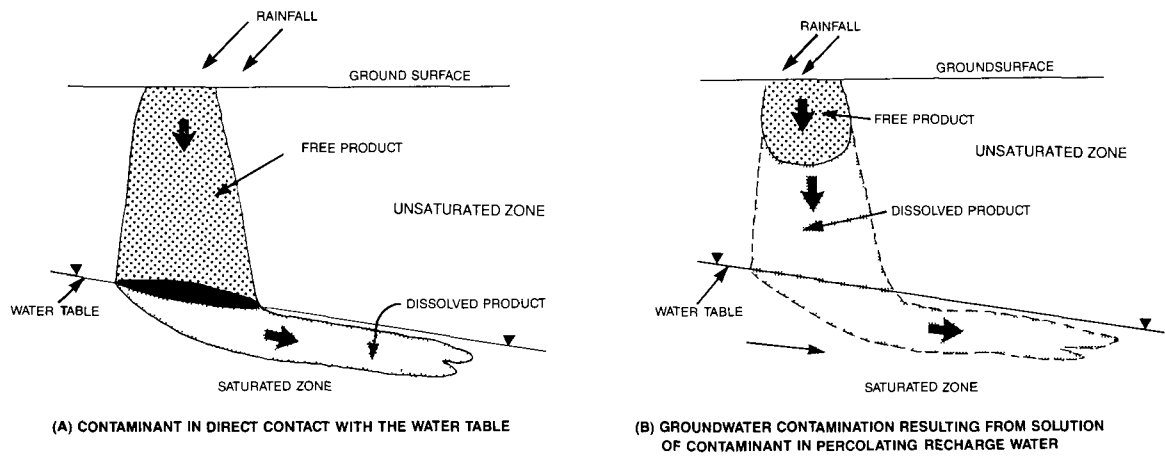
Figure 3. Schematic contaminant plumes showing methods by which groundwater can be contaminated.
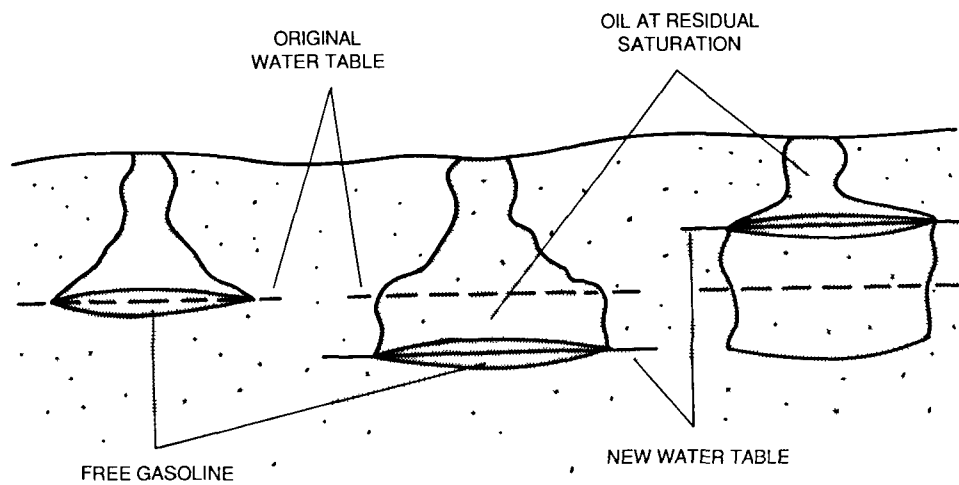
Figure 4. Contaminating effect on soil caused by fluctuating water table.

Vapor Transport in the Unsaturated Zone

Vapor phase transport of gasoline components in the unsaturated zone can pose a significant health and safety threat because of inhalation and explosion potential.

For vapors to move in the unsaturated zone, the soil and rock formations must be sufficiently dry to permit interconnection of air passages among the soil pores. Two parameters then govern movement: vapor concentration and vapor flow. Leaked gasoline will have its greatest vapor concentration at the leak site, where the free gasoline is evaporating at the liquid-vapor interface. The rate of vaporization depends on the vapor pressure of the gasoline constituents, the pore pressure and moisture content of the soil, and the ambient temperature. The natural vapor flow (or flux) is away from areas of high concentration to areas of lower concentration and ultimately to the atmosphere. In warm weather, vapors of benzene, toluene, or xylene (BTX) readily escape upward by diffusion. If there is an impermeable layer above the rising vapors, however, such as a paved road, building, or parking lot, or if the ground surface is frozen, the vapors are able to move only by lateral underground travel; thus, migration can occur over relatively long distances.

The principal modes of gasoline vapor transport in soils are diffusion and advection. Diffusion is the mass transport that results from the random motion of vapor molecules and is generally away from areas of high concentration towards areas of low concentration. Advection results from changes in the total pressure gradient and is the net downgradient migration of gases. Pressure changes that cause advection vapor movement result from barometric pumping, imposed pressure gradient, and density differences.

Barometric Pumping

Pore air pressure deep in the unsaturated zone typically reflects the mean atmospheric pressure at the ground surface. A rise or fall in atmospheric pressure with respect to the pore pressure will result in vapor flow into or out of the soil. This mechanism is most important where the depth to the free gasoline is small compared to the depth of the unsaturated zone. It can increase the rate at which the free gasoline volatilizes.

Imposed Pressure Gradient

In cold weather, a heated basement may cause the density of the column of air in the building to be less than that found outside in the ground. In addition, the action of a furnace draws air into the basement from the surrounding subsurface. Vapors will seep into a basement from the soil pores through pathways such as cracks in basement walls, unfinished floors, or crawl spaces.

Density Differences

If a vapor has a density sufficiently different from that of other gases in the soil pores (such as air), there will be a gravity-driven density current of the vapor. In particular, a relatively heavy vapor will tend to "pour" down to the bottom of the unsaturated zone and pool as a lens on top of the water table (or on top of another lens of even denser vapor).

A number of soil treatment techniques can be used to collect vapor emissions or enhance volatilization. These and other technologies are discussed in Section 4.

Gasoline Degradation in the Subsurface

Gasoline compounds that reach the subsurface are subjected not only to the physical processes of dissolution, adsorption, and volatilization, but also to chemical processes. The most important of these are biotic and abiotic chemical transformation.

There are two biotic processes: biodegradation and biotransformation. These processes are oxidation-reduction reactions performed by microorganisms. Biodegradation is the decomposition of a contaminant by microorganisms such as bacteria, fungi, and yeasts. The end products of biodegradation are water, carbon dioxide, and energy for cellular growth and reproduction. Biotransformation is the partial biodegradation of compounds. In biotransformation, contaminants are partially degraded to simpler compounds which may be more or less soluble or toxic than the original compounds.

Abiotic chemical transformations are reactions—not performed by bacteria—that decrease contaminant concentrations by degrading the chemicals into other products. The most important chemical transformations are hydrolysis and oxidation/reduction reactions.

In the subsurface, both aerobic (meaning in the presence of oxygen) and anaerobic (in the absence of oxygen) conditions exist. Biodegradation occurs under both conditions; however, for most gasoline components, the rate of decay is greater under aerobic conditions. Other parameters that can influence the rate of biodegradation include: soil moisture content, compound availability, oxidation/reduction potential of the compounds, ambient temperature, pH of soil, inorganic nutrients, and concentration of microorganisms (Fleischer, 1987).

Degradation is often the result of the combined effects of chemical transformations and biodegradation. For example, the oxidation/reduction of complex hydrocarbons can produce simple compounds such as peroxides, primary alcohols, and monocarboxylic acids. These compounds can then be further degraded by bacteria, leading to the formation of carbon dioxide, water, and new bacterial cell materials (CONCAWE, 1979).

Summary

- The migration of gasoline through the subsurface depends on the quantity released, the multiphase flow characteristics of the individual gasoline compounds, and on the structure of the soil and rock formations through which the gasoline moves.

- Gasoline compounds in the subsurface may be partitioned by phases: as free product retained in pore spaces and floating on the water table, adsorbed to soil particles, as vapor in soil and air, and as dissolved compounds in soil water. These multiphase characteristics are determined by the physical and chemical properties of the compounds. For example, benzene, toluene, and xylene are highly volatile and, therefore, are commonly found in the vapor phase; naphthalene and ethylbenzene exhibit relatively low solubilities and vapor pressure and, therefore, are most common in the free product phase; and phenol is highly soluble in water, has relatively low vapor pressure, and is therefore common in the dissolved phase.

- As gasoline moves through the unsaturated zone, it migrates both vertically (downward) and horizontally. The vertical component is due to gravity, while the horizontal component is due to capillarity. Gasoline transport in the unsaturated zone is a multiphase phenomenon: free product migrates through the zone or is held in pore spaces; gaseous product or vapor moves in the soil air; and dissolved product moves in soil water and adsorbs to soil.

- Gasoline movement in the capillary zone is limited to lateral spreading. As gasoline accumulates on the water table, it forms a lens that moves horizontally with the groundwater gradient. The free product phase continues to migrate until it is completely adsorbed to soil and rock particles and residual saturation is reached. The dissolved phase flow occurs as compounds move into solution from the free product phase.

- The transport of gasoline components in the saturated zone is limited to the dissolved phase. Solutes enter the groundwater and move in the general direction of the groundwater gradient according to the mass transport laws of advection and dispersion.

- A gasoline compound in the free product phase will enter the vapor phase according to its specific vapor pressure (the higher the vapor pressure of the compound, the more likely it is to volatilize). Once in the vapor phase, the contaminants will move by advection and diffusion. Vapor phase transport poses a significant health and safety threat because of inhalation and explosion potential.

- Gasoline components are degraded in the subsurface by biotic and abiotic chemical transformation processes. Biotic processes include biodegradation and biotransformation by microorganisms. Abiotic chemical transformations include hydrolysis and oxidation reduction reactions. Degradation by microorganisms occurs in both aerobic and anaerobic environments; however, for most gasoline compounds the rate of biodegradation is higher under aerobic conditions (i.e., in the unsaturated zone).

Numerous treatment technologies are available to remove gasoline from air, soil, and water. Detailed discussions of some of them are presented in the following sections. Section 3 covers treatment technologies for removing free product from the water table; Section 4 covers gasoline adsorbed in the unsaturated zone; and Section 5 covers gasoline dissolved in groundwater.

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Section 3
Recovering Free Product

The principal means of recovering floating contaminants from the groundwater surface is the use of the natural water gradient to control the movement of the contaminants. This is accomplished either by inducing a water gradient or by influencing an existing one artificially. Pumping wells and trenches are the devices most commonly used to influence the flow of groundwater.

Pumping wells sunk several meters below the water table surface remove water from the aquifer, creating depressions in the water table into which floating oil and gasoline accumulate. Trenches dug perpendicularly to a groundwater gradient intercept the flow of floating contaminants. Once enough floating free product has accumulated in a water table depression or a trench, it can be recovered with skimmers, filter separators, or special pumps.

The use of pumping wells and trenches to influence the flow of an aquifer minimizes the threat to adjacent groundwater bodies and soil by containing the spread of floating free product. Also, by accumulating floating product in water table depressions and trenches, both free product and dissolved constituents can be removed. It should be noted that a basic understanding of the hydrogeology and soil characteristics at the site and the extent of the spill is essential to the effective recovery of floating free product.

In this section, the different methods of free product recovery and available types of oil/water separation equipment are discussed and analyzed for cost, efficiency, and limitations. The information presented is based on contacts with groundwater consultants, with free product recovery equipment designers and technicians, and on Camp Dresser & McKee Inc.'s experience.

Methods of Gasoline Plume Containment

Trench Method

One of the simplest free product recovery strategies is to dig a trench with a mechanical excavator down to the water table and intercept the flow of the floating gasoline. This method is applicable only when the water table is relatively shallow and the gasoline plume is less than 10 to 15 ft below the ground surface. Once the groundwater flow direction and plume size have been established, a trench is dug in the path of the migrating plume. The trench is dug deep enough so that the groundwater "ponds" and the floating gasoline is exposed (Figure 5). To increase the flow of gasoline to the trench, water in the trench below the surface may be pumped out. In doing so, a hydraulic gradient is created, more groundwater is pulled toward the trench, and the aquifer is induced to redirect the movement of the floating gasoline. To ensure that the intercepted gasoline does not escape back into the soil, an impermeable membrane can be placed on the downgradient side of the trench. The membrane can serve as a baffle preventing the flow of gasoline but allowing water to pass under it.
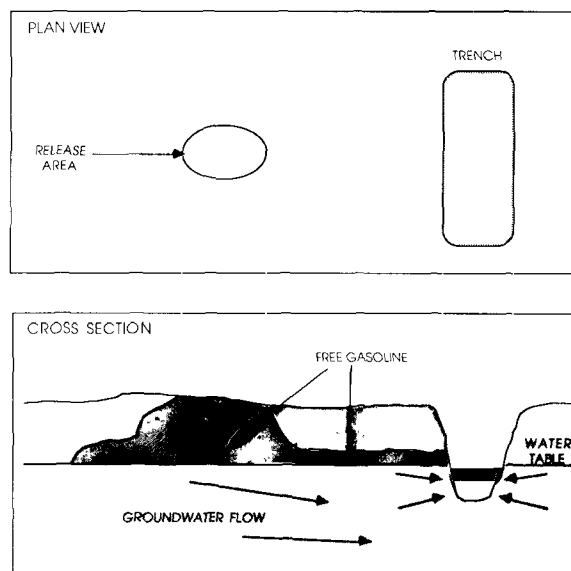

Figure 5.   The trench method of recovering free product.

Gasoline ponding in the trench can be removed with a variety of portable, free-floating contaminant recovery devices. Some equipment, such as filter separators, work automatically only when gasoline is present in the trench, separating and removing the gasoline from the water. Other devices include hand-held skimmers, which are no more than sophisticated floating vacuum cleaners with hydrocarbon sensors. In cases where both gasoline and water are pumped out of the trench, standard gasoline recovery equipment can be used. Large, nonportable oil/water separation tanks, like those used for industrial applications and at gasoline and oil refineries, are commonly used. (For further discussion, see Gasoline Recovery Equipment, p. 18).

For the trench method to be implemented successfully, the groundwater and soil conditions must be favorable. The water table should be high (i.e., less than 10 to 15 ft below the ground surface), and the soil above the water table must be firm and well aggregated so that the trench is self-supporting. Temporary trenches may not need support to prevent the trench from caving in, but for long-term recovery the trench may be partially backfilled with crushed stone and coarse gravel on the sides, or supported with plywood siding or concrete slurry walls. As a rule, a wide trench has no particular advantage over a narrow one. But in general, the longer the trench, the faster it will collect gasoline, provided that the water table is kept depressed.

Pumping Well Method

For sites with wells or with a water table that is too deep for trenches to be effective, well pumping strategies are used to influence the aquifer and recover gasoline spilled on the groundwater surface. Once the characteristics of the aquifer have been established and the direction of groundwater flow and size of plume are known, water pumping rates can be calculated which will contain the migration of the contaminant plume. Groundwater models and other analytical techniques are available to assist in the proper siting and sizing of containment wells. If a single well and the "cone of influence" or depression it produces are not sufficient to contain the spread of the plume, multiple wells may be drilled. The wells should be positioned with respect to the plume and in proximity to one another in such a way that the cones of influence overlap and thereby prevent the migration of the plume beyond the influence of the wells (Figure 6).

Single Pump Systems

In a single pump system, both gasoline and water are recovered through a single pipeline to above-

ground storage tanks or oil/water separators (Figure 7). Two problems are associated with single pump systems: (1) large volumes of contaminated water must be stored, treated, and disposed; and (2) during pumping, gasoline and water are mixed, thereby complicating aboveground separation. For these reasons, single pump systems are most commonly employed for smaller spills when the gasoline-water recovery rates are relatively low (e.g., less than 500 gal/h).

Dual Pump Systems

In cases where large amounts of gasoline must be recovered, two pump systems are frequently employed. Dual pump systems using separate gasoline and water pumps facilitate separation of gasoline and water in the well, thus significantly reducing the amount of water that must be treated. As in the trench method, water pumps are lowered into the wells up to depths of 10 to 15 ft below the water table surface. The pumps draw in water from all directions and establish a cone of influence or depression in the water table. Floating gasoline is drawn into the depression where it can be recovered as free product with a product recovery pump (Figure 7).

The "water table depression pump," as it is called, should maintain a constant, or nearly constant, cone of influence to prevent the migration of the gasoline plume. If a constant depression is not maintained and the water table and the gasoline plume are allowed to rise, gasoline droplets may adhere to soil particles. As the water table continues to rise, the density differential between the gasoline and water would not be great enough to overcome the adhesive forces of the soil particles, and the gasoline droplets would remain in the soil. If the cone or depression is allowed to recover completely, the gasoline plume will once again be free to migrate along the natural groundwater gradient.

Dual pump systems operate in the following way. Initially, the water table depression pump probe is set at an arbitrary depth in the well to which the water table will be depressed. The water table depression pump is then lowered approximately 10 ft beyond the probe and pumping is begun. As water is pumped out of the well, the water table and floating product are drawn down until the water pump probe detects the presence of hydrocarbons. When this occurs, the water pump will cease pumping and the depressed water table will rise slightly. As soon as the water pump probe detects water again, however, it will resume pumping and the depression will be maintained. Once a constant depression has been established, the product pump is deployed.

DIRECTION OF
GROUNDWATER FLOW

SPILL SITE

Recovery Well

Recovery Well

Recovery Well

Recovery Well

Recovery Well

EXTENT OF
GASOLINE PLUME

EXTENT OF CONE
OF INFLUENCE
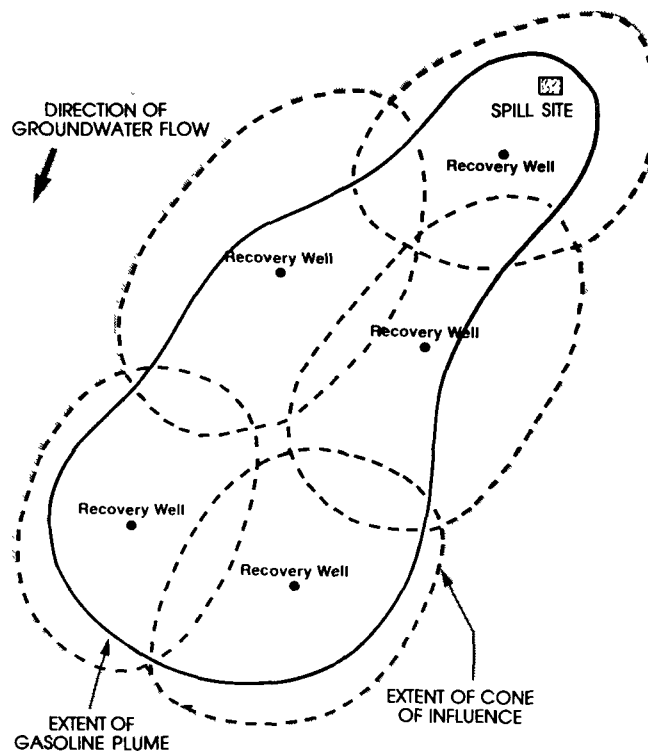
Figure 6.   Using overlapping cones of influence to contain gasoline plume.

SINGLE PUMP SYSTEM

OIL-WATER SEPARATOR

OIL

WATER

GAS
SPILL

UNSATURATED
ZONE

STATIC   WATER LEVEL

AQUIFER

WATER LEVEL
WHEN PUMPING

CONCENTRATED
FREE PRODUCT

GASOLINE-WATER
PUMP

DUAL PUMP SYSTEM

UNSATURATED
ZONE

GAS
SPILL

WATER TABLE

AQUIFER

CONCENTRATED
FREE PRODUCT

PRODUCT RECOVERY PUMP
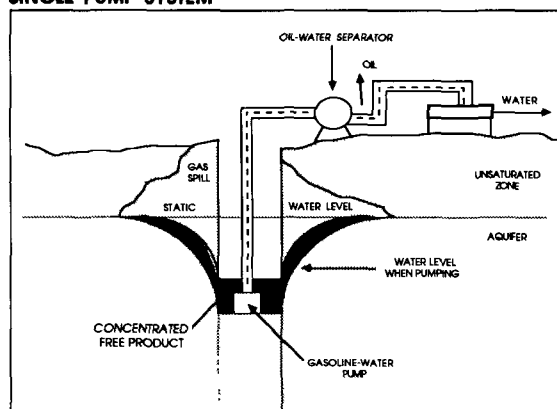
WATERTABLE
DEPRESSION PUMP

Figure 7.   Single pump and dual pump gasoline recovery systems.

The inlet and probe of the product pump are set at the same depth, a few inches above the probe of the water table depression pump. As the water pump draws in groundwater, gasoline will accumulate in the depression until the hydrocarbons are detected by the product pump probe.

The probe of the product pump has the same function as the probe of the water table depression pump: it activates the pump when gasoline is present and turns the pump off when the gasoline plume reaches an arbitrary minimum thickness or when the water table fluctuates and water is detected.

In addition to limiting the amount of water that must be treated, the dual pump system has another advantage over the single pump system: the dual pumps function automatically. Barring equipment failures, water table depression and product removal are constant, and the system can operate for weeks or months with only periodic inspections. Once the gasoline plume has been drawn down to within a fraction of an inch, the product pump probe will no longer be able to detect the remaining gasoline. At this point, the product pump turns off, and the water table depression pump is elevated to the depression and allowed to pump the mixture of water and the remaining gasoline out of the well. When the levels of contaminants in the recovered gasoline-water mix have dropped to acceptable water quality limits, pumping is terminated and the well is considered clean.

It should be noted that in order to achieve drinking water quality standards, considerable amounts of money and technological resources must be invested in the cleanup. Some sites could take years to restore depending upon the complexity of subsurface conditions and the volume of gasoline spilled.

Limitations

Although trenches are commonly employed as an effective means of containing the spread of subsurface spills, there are limitations associated with their construction and use. The most serious limitation is that trenches are feasible only when the water table is relatively shallow and the floating free product is less than 10 to 15 ft below the ground surface. The cost of the trench excavation and materials (for example, concrete slurry walls and riprap to support the walls of the trench, and gasoline-impermeable liners to prevent the flow of gasoline through the downgradient side of the trench), increases significantly with depth. Below 10 to 15 ft the cost of the trench method becomes more than the cost of using other containment methods, for example, the pumping well method.

Another limitation is the problem of extracting the free product once it enters the trench. Pumping and skimming must be continuous to maintain a flow gradient to the trench. Otherwise, the floating free product will tend to move to the ends of the trench and pass around the impermeable liner. When using only pumps to extract the gasoline-water mix, rather than including skimmers and filter separators to perform in situ free product recovery, aboveground storage and separation of the trench liquids may pose problems. For example, storage and transportation of the gasoline-water mix requires special handling precautions; likewise, purchasing or renting an oil/water separator, or finding a suitable disposal alternative for the gasoline-water mix will considerably increase the costs of free product recovery.

Gasoline Recovery Equipment

In the United States, more than 25 companies design and sell equipment and provide technical advice on gasoline recovery from subsurface spills. Many of the companies deal strictly in aboveground oil/water separators such as those typically used at petroleum refineries and wastewater treatment plants. Others have created their own lines of in situ oil/water separation devices specifically designed to separate oil and water underground and recover free product. Site-specific, state-of-the-art equipment is available which can recover free product from a variety of adverse subsurface conditions. There are narrow pumps for small wells, filter separators which operate passively, and special dual pump systems for deep wells. Yet, even as designers produce new and improved equipment, none claim that their oil/water separation equipment can recover 100 percent of the spilled product.

It is an accepted fact that a certain percentage of the spill will always be trapped in the unsaturated soil as the plume migrates from the spill site to the water table. Only the portion of the original spill that ends up as free product on the water table is readily recoverable.

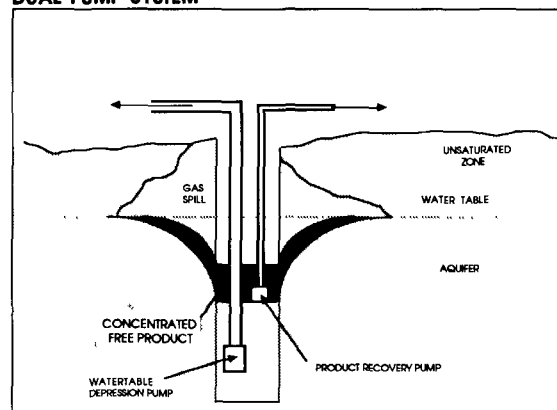The following subsection is a discussion of the different types of oil/water separation equipment available for recovering gasoline that has reached the groundwater table. The equipment is evaluated for ease of operation, removal efficiency, limitations, and cost. For more detail on the pumps and recovery equipment available on the market, see Tables 4 through 8 at the conclusion of this discussion.

Skimmers and Filter Separators for Trenches

Skimmers

Skimmers are designed to float and automatically pump gasoline off the water surface. The most effective skimmers are equipped with conductivity sensors to detect gasoline. When gasoline-free water is present, an electric signal is passed between the sensors, and the gasoline pump does not operate. But when gasoline, which is nonconductive, is present, the electric signal is interrupted and the pump is automatically turned on. The pump extracts gasoline from the trench until clean water is detected by the sensors. Skimmers are easily deployed and may be set up temporarily or permanently, or they may be attached to a handle and operated manually.

For manually operated skimmer equipment, the gasoline recovery pump is not attached to the floating sensor. Rather, it is set on the ground above the trench and connected to the skimmer with a synthetic hose to remove the gasoline. A 1/4-hp pump can recover product at a rate of 2.8 gal/min or 4,000 gal/d.

One advantage of skimmers is that they can pass grit and debris up to a quarter of an inch thus allowing unfiltered gasoline to be recovered. Once the skimmed product has been removed from the trench, it is stored in recovery drums for further treatment or disposal. Skimmers can recover water-free gasoline to the limit of the sensor's ability to distinguish gasoline from water (usually at a depth of a fraction of an inch). Then, with the gasoline sensor turned off, skimmers suck up the remaining gasoline mixed with small amounts of water from the water surface of the trench. The average capital cost of a skimmer is $6,000 to $7,000, but combined with a water table depression pump to increase the flow of gasoline to the trench, a skimming system could cost as much as $12,000 to $13,000.

Filter Separators

Like some of the skimmers, filter separators float on the trench water surface and pump gasoline automatically and continuously. Yet, unlike skimmers, which operate with the aid of conductivity sensors, filter separators have special filters that allow gasoline and other petroleum products to pass but repel water. The filter separator floats so that the oleophilic-hydrophobic ("oil-loving"—"water-hating") membrane is positioned at the gasoline-water interface. Both gasoline and water contact the filter, but only the gasoline moves through. Once a small amount of gasoline (approxi-

mately one liter) has accumulated within the separator's compartment, a floating arm is raised which sends an electric signal to activate the gasoline recovery pump and the compartment is automatically drained.

The gasoline recovery pump is located above the trench and is connected to the filter separator with a gasoline-resistant hose. A 1/4-hp pump can remove gasoline from the separator at a rate of 5 gal/min. Filter separators of this kind are portable and easily installed, and can reduce a gasoline plume in a trench down to a sheen. They generally cost about the same as skimmers ($6,000 to $7,000), but if a water table depression pump is required, the filter separator system could cost as much as $12,000 to $13,000.

Filter Separators and Dual Pump Systems for Shallow Wells

Filter Separators

The same type of filter separators that are used for trench equipment may be used in shallow wells. The design and operation of the unit are the same, but there are more variables to consider when using filter separators in shallow wells.

It should be noted that pumps are generally classified according to their pumping position with respect to the well structure, regardless of the depth of the well. A pump installed above a well is called a shallow well pump, and a pump below the ground surface inside a well is called a deep well pump. This means that it is possible to have shallow well pumps pumping from greater depths than deep well pumps. To avoid confusion in this handbook, shallow wells are defined as wells in which the depth from the top of the well to the liquid surface is less than 20 ft, and deep wells are wells in which the depth from the top of the well to the liquid surface is greater than 20 ft.

The first consideration when using filter separators is that they be deployed only to a maximum depth of 20 ft. Although the separation unit floats on the water table surface, its surface-mounted pump is physically unable to provide more than 20 ft of lift (head). To achieve greater pumping heads, submersible pumps would be needed, but submersible pumps cannot be attached to filter separators because the heavy pump would cause the floating separator to sink. Therefore, filter separators can be used only with surface-mounted pumps in shallow wells. (For more detail, see Dual Pump and Single Unit System for Deep Wells, p. 20.)

A second consideration when using a filter separator is maintaining a steady flow of gasoline to the separator. This is done by deploying a water table depression pump below the groundwater sur-

face. The pump removes water from the well, creating a depression in the water table. The floating gasoline flows into the recovery well and accumulates on top of the depression where it can be easily separated by the filter.

Filter separators are more difficult to deploy in shallow wells than in trenches because a water table depression pump is required. A cone of influence must be maintained to trap the floating gasoline and, as a result, the system is more expensive and requires more time and supervision to achieve and maintain conditions amenable to the filter separator. Gasoline removal efficiencies of filter separators in shallow wells are comparable to filter separators in trenches. In both cases, the filter separator can reduce the gasoline plume to a sheen on the water table. To achieve additional recovery, the top layer of gasoline and water must be removed from the well and treated aboveground.

Dual Pump Systems

Of all the oil/water separation equipment available on the market, dual pump systems composed of water table depression pumps and product recovery pumps are the most common. In all cases, the water table depression pumps are designed to pump water out of the well and thereby create depressions in the water table into which floating free product accumulates. The product recovery pumps are designed to pump water-free gasoline out of these depressions. Dual pump systems come in a range of sizes and pumping capacities to meet a variety of well diameter, depth, and pumping conditions. Water pumps come in sizes as small as 3 1/2-in diameter for 4-in wells and as large as 10-in diameter for 12-in and 24-in wells. Water pumps range in pumping capacity from 1/3-hp units, which have a maximum pumping rate of 15 gal/min and a maximum total dynamic head (TDH) of 130 ft, to 7 1/2-hp units with a maximum pumping rate of 230 to 500 gal/min and a maximum TDH of 300 ft. Product recovery pumps come in similar sizes and pumping capacities, though, as a rule, they are not required to do as much pumping as water table depression pumps.

Water table depression pumps and product recovery pumps are equipped with sensors which allow them to pump only pure product. As the free product is removed from the water table depression and the lens of gasoline becomes too thin for the product recovery pump sensor to detect, water-free gasoline recovery will cease. To remove the remaining portion of the gasoline lens, as well as the gasoline constituents dissolved in the groundwater, the top layer of water in the well is pumped out to bring a mixture of gasoline emulsions, dissol-

ved materials, and water to the ground surface. Once the level of constituents in the groundwater is within acceptable limits, the well is considered clean and pumping is terminated.

Dual pump systems are capable of removing up to 99 percent of the free product and dissolved gasoline constituents from groundwater. One hundred percent removal is impossible because dissolved constituents migrate both vertically and horizontally away from the plume and are therefore dispersed through a much greater volume of water than is the undissolved free product. Furthermore, as aquifer recharging and water table fluctuations occur, gasoline emulsions and dissolved constituents trapped in the soil may make their way down to the aquifer, thus further contaminating it.

Dual Pump and Single Unit Systems for Deep Wells

The technology of deep well pumps is different from that of shallow well pumps. When the pumping level in a well exceeds 20 ft, physical restrictions limit the type of pumps that can be used. Surface-mounted pumps, which rely on atmospheric pressure to provide suction lift, have a theoretical maximum lifting capacity of 34 ft. Beyond 34 ft, the pull of gravity exerted on the rising liquid column exceeds the capacity of the pump to provide lift. In practice, the 34-ft theoretical maximum is never achieved—20 ft is the highest lift that can be expected with surface-mounted pumps. As a result, submersible pumps must be used in wells where pumping water depths exceed 20 ft. Submersible pumps do not rely on suction lift; rather, they are submerged in the well, below the liquid surface and, with the aid of pistons, rotors, vertical turbines, jets, or compressed air, they push the liquid out of the well.

Surface-mounted pumps have three distinct advantages over submersible pumps: (1) they are easier to operate and maintain because they are aboveground; (2) they are generally less expensive (submersible pumps must be made explosion-proof due to the presence of volatile hydrocarbons and also must be able to pump in corrosive environments); and (3) they generally have a longer lifespan (on average, two to three years longer than submersible pumps, which are exposed to gasoline, oil, and other corrosive chemicals).

Dual Pump Systems

Dual pump systems for deep wells operate generally in the same manner as dual pump systems for shallow wells. Two pumps are employed. A water table depression pump contains the migration of the gasoline plume, and a product recovery pump

draws off the gasoline that has accumulated in the water table depression. The two pumps are usually set some 10 to 15 ft apart to ensure adequate draw-down and to ensure that the water table depression pump does not come in contact with the gasoline. Each pump is equipped with its own sensor to prevent the pumping of gasoline-water mixtures, and each is operated independently so that a constant depression in the water table is maintained while gasoline is being recovered.

The main difference between dual pump systems for deep wells and shallow wells is that in deep wells greater pumping distances and more extreme pumping conditions are found, requiring more powerful, durable pumps. Water table depression pumps and product recovery pumps are available that can pump from depths as great as 500 ft and can withstand the corrosive effects of saltwater and water laden with sediments. The 2- and 3-hp water table depression pumps commonly used in deep well recovery operations are rated to pump a maximum of 60 gal/min and have a maximum head of 150 ft. Product recovery pumps used in deep wells are seldom required to pump as much as water table depression pumps and therefore have lower ratings.

Another important distinction between dual pump systems for deep and shallow wells is that surface-mounted, suction lift pumps cannot be used, since deep wells (as defined here) are wells in which pumping depths exceed 20 ft. Only submersible pumps can be used in deep wells. Moreover, due to their greater pumping capabilities and other features that allow operation under adverse conditions (for example, explosion-proof drive units, water-tight seals, electric cables), deep well submersible pumps are more expensive than surface-mounted pumps. On the average, submersible pumps are 10 to 15 percent more costly than surface-mounted pumps. As a result, dual pump systems for deep wells are more expensive than dual pump systems for shallow wells.

Another economic distinction between shallow well and deep well recovery systems is seen in well drilling costs. As Table 3 shows, drilling costs increase linearly with depth.

Costs include engineering and labor, and it is assumed that the wells are auger-drilled and gravel-packed, and that they have galvanized steel, gasoline-resistant screens. It is also assumed that the wells are drilled in sandy-gravel soil and that the wells yield pumping rates of 20-100 gal/min. These cost figures were taken from a survey of practicing drillers.

Table 3
Well Drilling Costs

Diameter	Cost/ft
4-in.	$ 90-120
6-in.	$100-130
8-in	$120-160
10-in	$150-200
24-in	$300-350

A 4-in well drilled to 20 ft costs $2,100, while the same size well drilled to 40 ft costs $4,200. The diameter of the well also affects cost. As Table 3 indicates, the larger the diameter of the well, the greater will be the per-foot drilling costs. For example, an 8-in well costs, on the average, $35 more per foot to drill than a 4-in well, while a 10-in well costs about $70 more per foot than a 4-in well.

Well drilling costs are important because they influence the treatment options available at the site. Unlike recovery equipment costs, which increase only moderately with incremental changes in design capacity, well drilling costs show steep increases with slight changes in diameter and depth and may, in some cases, exceed the costs of the recovery equipment. For this reason, when recovery options are being considered, close attention should be paid to optimizing drilling and recovery costs.

Single Unit Systems

In wells with limited access, such as small diameter wells, single unit dual pump systems can be deployed. Single unit systems equipped with both water table depression and product recovery pumps are available to fit wells as narrow as 4 in. in diameter. The product recovery pump is attached above the water table depression pump, and both pumps are equipped with sensors that control pumping in the same manner as described above for dual pump systems. Single unit dual pumps for narrow wells have low pumping rates (i.e., 0.6 gal/min at a maximum depth of 160 ft), but they sell for as little as $12,000.

Table 4
Product Recovery Equipment for Trenches

Company/Product	Dynamic Head (ft)	Pumping Rates (gal/min)	Degree of Oil/Water Separation	Advantages	Disadvantages	Cost[1]
ORS[2] Scavenger	< 20	< 5	Sheen	Lightweight, portable, passive filter separator (does not require energy inputs for separation), automatic product pump	Maximum pumping distance 20 ft	$6,850
ORS Tramp Oil Scavenger	< 70	< 2.8	99% +	Pumps product automatically, can be operated manually or deployed permanently, pneumatic pump can pump thick oil grit		$6,850

[1] Costs are for equipment only and do not include installation
[2] Oil Recovery Systems, Inc., Norwood, MA.

Table 5
Product Recovery Equipment for Shallow Wells (Water Table ≤ 20 ft)

Company/Product	Dynamic Head (ft)	Pumping Rates (gal/min)	Degree of Oil/Water Separation	Advantages	Disadvantages	Cost[1]
ORS[2] Scavenger	< 20	< 50	Sheen[3]	Lightweight, portable, passive filter separator (does not require energy inputs for separation), automatic product pump	Requires 24-in well, maximum pumping distance is 20 ft	$6,850
ORS Probe-Scavenger	15-80	8-38	99% +[4]	Smaller than Scavenger, submersible, greater pumping capacity	Requires 8-in well	$6,750
ORS Shallow Well	20-90	5-35	99% +	Can be used in wells as narrow as 3½ in, submersible		$6,750
EMTEK[5]-VP-1075-VCP	6-50	74-10	99% +	Can withstand adverse pumping conditions, can be used in wells as narrow as 6 in		$6,560
NEPCCO[6] Petropurge	5-85	40-0.5	99% +	Submersible, minimum well size is 4 in		$5,950

[1] Costs are for equipment only and do not include installation.
[2] Oil Recovery Systems, Inc., Norwood, MA
[3] Less than 1mm thick.
[4] Of the total hydrocarbons floating on the water table, 99 percent can be recovered Some water containing dissolved constituents can also be recovered, but it is impossible to remove all the dissolved constituents from the groundwater.
[5] EMTEK, Inc., Amherst, NH.
[6] NEPCCO, Foxboro, MA.

Table 6

Water Table Depression Equipment for Shallow Wells (Water Table ≤ 20 ft)

Company/Product	Dynamic Head (ft)	Pumping Rates (gal/min)	Advantages	Disadvantages	Cost[1]
ORS[2] Probe/Pump	15-35	70-10	Submersible, designed for Probe-Scavenger		$3,950
ORS Stainless-Steel Water Table Depression Pump	50-100 (½ hp) 50-125 (¾ hp)	50-12	Can be exposed to saltwater, maintains uniform depression	Requires 8-in well	$4,850
ORS Shallow Well Water Table Depression Pump	15-26	30-10	Can fit in 3½-in well, can be used in corrosive environments, surface-mounted	For shallow water table only	$4,150
EMTEK[3]-WP-1075 (¾)	6-50	74-10	Surface-mounted, can withstand adverse pumping conditions, minimum well size is 6 in		$3,736
NEPCCO[4] HP 1-9	93-190	7-1	Submersible, minimum well size is 4 in		$3,950
NEPCCO HP 4-6	60-130	28-10	Submersible, minimum well size is 4 in		$5,950

[1] Costs are for equipment only and do not include installation.
[2] Oil Recovery Systems, Inc., Norwood, MA
[3] EMTEK, Inc., Amherst, NH.
[4] NEPCCO, Foxboro, MA.

23

Table 7

Product Recovery Equipment for Deep Wells (Water Table > 20 ft)

Company/Product	Dynamic Head (ft)	Pumping Rates (gal/min)	Degree of Oil/Water Separation	Advantages	Disadvantages	Cost[1]
ORS[2] 4-in Scavenger	10-160	0.8-0.6	99% +	Water and gasoline pumps are together in one unit, can operate in 4-in well, can be deployed as far as 180 ft, submersible	Rates low pumping	$12,000
ORS Probe-Scavenger	15-80	38-8	99% +	Is also used for shallow wells, submersible	Requires 8-in well	$6,750
EMTEK[3]-PPSA-112	6-80	40-5	99% +	Submersible pump	Requires 8-in well	$5,950
NEPCCO[4] Petropurge	5-85	40-0.5	99% +	Submersible, minimum well size is 4 in		
NEPCCO-Narrow Well Petropurge	Not available	Not available	99% +	Submersible, pump is 3 in. in diameter		$6,375

[1] Costs are for equipment only and do not include installation.
[2] Oil Recovery Systems, Inc., Norwood, MA.
[3] EMTEK, Inc., Amherst, NH.
[4] NEPCCO, Foxboro, MA.

24

Table 8

Water Table Depression Equipment for Deep Wells (Water Table > 20 ft)

Company/Product	Dynamic Head (ft)	Pumping Rates (gal/min)	Advantages	Disadvantages	Cost[1]
ORS[2] Probe/Pump	15-35	70-10	Submersible	Maximum pumping distance is 40 ft	$3,950
ORS Stainless-Steel Water Table Depression Pump	50-150 50-125	60-25 2 (hp) 100-5 (3 hp)	Can be exposed to saltwater, submersible	Requires 8-in well	$6,950 $7,850
EMTEK[3] WP-1075-SHH	80-160	28-11 (¾ hp)	Submersible, multistage certified pump, can withstand corrosive environments	Requires 8-in well	$3,291
NEPCCO[4] HP 1-9	93-190	7-1	Submersible, minimum well size is 4 in	Low pumping rates at high heads	$3,950
NEPCCO HP 4-6	60-130	28-10	Submersible, minimum well size is 4 in		$4,175

[1] Costs are for equipment only and do not include installation.
[2] Oil Recovery Systems, Inc., Norwood, MA.
[3] EMTEK, Inc., Amherst, NH.
[4] NEPCCO, Foxboro, MA.

Aboveground Oil/Water Separators

Aboveground oil/water separators can be used as an alternative to in situ gasoline and water separation with water table depression pumps and product recovery equipment. Oil/water separators are typically used at oil refineries and wastewater treatment plants, but they can also be used to treat groundwater that has been contaminated with hydrocarbons. The separators are little more than large tanks into which the hydrocarbon and water mixture is pumped. Their main function is to slow the flow of the incoming water and to allow gravity separation of the less dense hydrocarbon emulsions. Separators have been successfully used at many sites but seem to be most effective when the hydrocarbon spill is relatively small and the rate of water flow through the separator is slow enough to allow for complete separation.

Oil/water separators are composed of two or more chambers. The first (the inlet or preseparation chamber) is for the deposition of settleable solids, and the second (the separation chamber) is for the separation of liquids of dissimilar specific gravities and the removal of the lighter liquid from the heavier liquid. Hydrocarbon emulsions and water recovered from a well are pumped into the separator through the inlet nozzle. The high velocity flow is directed against a baffle that is sloped at a 45° angle to the inlet. The baffle slows and disperses the incoming flow into a diffuse cascade that tapers outward and spreads across the entire width of the separator. Once the flow moves beyond the baffle, its turbulence is significantly reduced and gravity separation and settling can begin.

Primary coalescence of hydrocarbon emulsions occurs in the preseparation chamber. The less dense hydrocarbon droplets rising with the density gradient collide and fuse with adjacent droplets. According to Stokes'law, the larger the diameter of the particle, the faster the rate of rise. Thus, as small droplets coalesce to form larger droplets, their upward vertical velocity increases. Separation will continue as long as turbulence is minimized because turbulence interferes with coalescence and separation by breaking large globules of hydrocarbons into smaller globules that are more easily dispersed into water.

In some separators the preseparation and separation chambers are partitioned by coalescing tubes or coalescing plates.Coalescing tubes stand vertically across the width of the tank and are coated with an oil-attracting, petroleum-based chemical. As droplets coalesce on the tube surface, larger droplets form which rise to the water surface.

Coalescing plates are also designed to enhance the separation of hydrocarbon emulsions, but their mode of operation is somewhat different from that of the tubes. Coalescing plates are composed of a stack of corrugated metal plates which rise at an angle up to the water surface and extend across the width of the tank. Water containing hydrocarbon droplets flows between the plates, which are about an inch apart. Droplets rising with the density gradient accumulate and coalesce on the underside of the plates, forming larger droplets with faster rising rates. At the same time, solid particles suspended in the water settle onto the top sides of the plates and move by gravity to the bottom of the separator.

As the separated hydrocarbons begin to accumulate on the water surface, emulsion-free water is directed away from the corrugated plates or tubes and enters the separation sections. This quiescent zone allows for further gravitational separation of the remaining hydrocarbon emulsions. Once a distinct product layer has developed, it can be recovered with filter separators, product recovery pumps, or rotary pipe skimmers. A rotary pipe skimmer is essentially a pipe with the top quarter removed. The pipe is bolted to the side of the separation chamber and runs across its width. The pipe is rotated manually into the flow causing the layer of hydrocarbons to enter the pipe opening. The skimmed hydrocarbons are poured into 30-gal drums for disposal or re-refining. When skimming is complete, the pipe opening is returned to the vertical position.

Some oil/water separators are built with an outlet zone for the discharge of clarified water. This third chamber is separated from the separation chamber by a partition that extends across the width of the tank and down a few inches below the water surface. The partition is designed to block the flow of the hydrocarbon layer while allowing emulsion-free water to move underneath to the discharge pipe.

Oil/water separators range from 100-gal units to 50,000-gal units, but they are sized to treat specific volumes of water. Typically, separators are built to hold 10 times the extraction rate of the well. For example, a well being pumped at a rate of 100 gal/min would require a 1,000-gal separator to ensure adequate separation of hydrocarbons from water. Water is retained in the separator for at least 10 to 12 min, which is the minimum time in which complete gravity separation can be achieved. By undersizing the separator or increasing the extraction rate from the well, the water flow rate through the separator increases, thus reducing the retention time. But this reduction in retention time decreases the efficiency of the separator and allows hydrocarbon emulsions to remain in the separator effluent.

Therefore, it is critical in the design of the system that the volume of the separator tank be at least 10 times the extraction rate from the well. Under optimum conditions, an oil/water separator can reduce the amount of hydrocarbon emulsions in water to 15 ppm (1 ppm = 1 mg/ L).

The cost of oil/water separators is a function of the design capacity of the tank. For instance, a 1,000-gal separator (designed to handle a well extraction rate of 100 gal/min) costs between $5,500 and $6,000; a 5,000-gal separator costs between $10,500 and $12,000; and a 10,000-gal separator costs between $15,500 and $17,500. The costs will vary depending on what additional features are purchased. Exterior corrosion protection, for example, will increase separator costs by 10 percent, additional coalescence units will increase costs by 20 to 30 percent, and sensors and automatic product recovery equipment will cost an extra $5,000 to $7,000.

Subsurface Installation of Oil/Water Separators

A recent innovation in using oil/water separators to recover free floating hydrocarbons from subsurface spills has been to install the separator unit below ground, flush with the water table.

The main advantage of this technique is that the gasoline plume, which moves with the groundwater gradient, can be intercepted and recovered with minimum energy input. The plume is trapped and directed to the separator influent nozzle with either a subsurface drainage network—similar to an aboveground municipal storm drain system—or with a dike and an impermeable membrane to retard the flow of the plume. Both water and the intercepted hydrocarbons move by gravity flow through the separator inlet and into the separator chamber. Once separation of emulsions from water has occurred and the gasoline plume has redeveloped at the top of the separator, it is recovered with a product recovery pump, and the emulsion-free water is allowed to flow through the discharge back to the groundwater.

Because underground installation of oil/water separators is a relatively new remedial technique, little cost information is available. Despite this lack of information, several noneconomic considerations may make underground installation advantageous. For example, underground installation reduces the likelihood that water will freeze in the separator, eliminates the evaporation of potentially dangerous volatile hydrocarbons, and saves aboveground space for other uses. The disadvantages include the problem of excavating a hole large enough and deep enough to install the separator at the water table, as well as the quality of the separator effluent, which normally has a residual dissolved concentration of 15 ppm.

Limitations

The main limitation of using pumping wells is that they are time-consuming to install and cannot always be deployed soon enough to contain the migration of rapidly moving spills. When implementing the pumping well method, a careful hydrogeologic investigation of the groundwater flow characteristics and spill size is needed to determine the optimum location and number of wells to contain the spill. Hydrogeologic investigations are lengthy procedures, however, and often require weeks and even months to complete. Likewise, once a well has been drilled and a water table depression pump has been installed, there is a lag period (dependent on the conductivity of the aquifer) between the start of pumping, the creation of the depression, and the containment of the spill. Therefore, in cases where rapid deployment of containment measures are required, other less time-consuming methods such as the trench method may be more suitable.

A second limitation associated with using the pumping well method is that the water table depression must be kept constant. If a constant depression is not maintained and the water table is allowed to fluctuate, gasoline droplets may adhere to soil particles and be trapped below the water table. If the depression is lost completely, the floating free product will once again be free to flow with the groundwater gradient. Likewise, if the depth of the depression is lowered, a greater volume of soil will be exposed to the gasoline plume and further contamination of unsaturated soil may result.

When using single pump systems to recover free product from the water table, two problems arise. First, since only one pump is used, large volumes of gasoline-laden water are recovered. Once the gasoline-water mix is pumped out of the well, it must be stored, treated, and properly disposed. The second problem is that gasoline and water become well mixed during pumping, further complicating the separation process. In northern climates, it is usually necessary to winterize free product recovery equipment. Ice can form inside oil/water separators and other types of equipment, thereby reducing their effectiveness.

Finally, caution must be exercised when digging trenches or drilling wells so as not to rupture underground utilities. Locations of water and sewer pipes, gas mains, electrical wiring, telephone cables and other types of underground conduits should be determined before excavation.

Disposal of Recovered Gasoline and Contaminated Water

Gasoline recovered from subsurface spills can be disposed of by incineration, or, in many cases, it can be reused with little or no treatment. If the disposal option is chosen, the gasoline must be stored and transported with care to ensure that no further spills occur. If the gasoline is to be reused, it must be re-refined or mixed with other gasoline because it degrades ("weathers") while in the soil.

The cumulative effects of three processes leads to the degradation of gasoline. In the presence of oxygen, aromatic hydrocarbons such as benzene, toluene, and xylene are oxidized; gasoline constituents are metabolized by soil microbes; and hydrocarbons are dissolved in water stored in soil pores and at the water table surface. If recovered and used immediately, weathered gasoline can cause pinging and knocking in automobile engines thereby necessitating blending or re-refining.

Recovered water that contains small amounts of floating free product and dissolved constituents must first be passed through oleophilic-hydrophobic absorbent filters to remove the remaining free product. Once the emulsions are removed, four options are available to dispose of the water and dissolved hydrocarbons. The first option is to recharge the aquifer with the recovered water in order to flush out the remaining pockets of free gasoline. The main drawback to this technique, however, is that the recharging water still contains dissolved constituents and by flushing the unsaturated zone, the constituents are merely recycled back into the groundwater.

The second option is to discharge the water to a natural water course where dilution and exposure to oxygen will reduce the threat posed by dissolved gasoline constituents. To do this, a National Pollutant Discharge Elimination System (NPDES) permit is required. At this writing, there are no established Federal water quality standards for discharging contaminated groundwater to natural water courses, although some states and local authorities have established their own standards for the quality of discharged groundwater. It is advisable that "best engineering judgment" be exercised and consideration be given to maintaining the quality of receiving waters when discharging.

The third option is to send the water through a wastewater treatment plant where adsorption systems can remove the remaining dissolved constituents. An obvious problem with this technique is whether sewer lines are available near the recovery well and whether the wastewater treatment plant can handle the increased flow.

The fourth option, to treat the emulsion-free water with on-site air strippers and carbon adsorption filtration systems, is the most expensive. Air strippers facilitate the volatilization of dissolved components by increasing the water surface area exposed to oxygen, and carbon adsorption systems adsorb dissolved constituents out of the water. Together, the two systems can reduce the level of dissolved constituents to within the range of most drinking water quality standards and produce highly potable water. For a further discussion of air stripping and carbon adsorption, see Section 5.

Conclusions

Before deciding which treatment options and recovery equipment would be most effective in remediating a subsurface gasoline spill, the characteristics of the site must be known. A hydrogeological investigation, complete with monitoring wells and chemical testing, is needed to determine the geology and soil characteristics of the site, the depth to the water table, the groundwater gradient, the size and migration patterns of the gasoline spill, and the thickness of the plume. Without this basic information, recovery operations could be severely hindered. The location of underground utilities must also be considered when drilling or digging.

Once the site analysis is complete, the most important consideration is how to contain the migration of the gasoline plume. In a shallow spill, it is usually possible to respond more rapidly and effectively with a trench than with a well system. The reason for this is that equipment and contractors for this type of installation are readily available in most areas, and recovery from trenches is less complicated.

Once the recovery method has been selected, the equipment must be considered. Skimmers, filter separators, surface-mounted product recovery pumps, and aboveground oil/water separators can all be used in recovering gasoline from trenches.

Another advantage of using a trench is that it can be dug long enough to intercept the entire plume, thus allowing complete aboveground recovery of free product. Aboveground recovery is desirable for several reasons. First, all the product recovery equipment is surface-mounted and is therefore easier to operate and maintain than submersible equipment. Second, more recovery equipment options are available (for example, filter separators, portable skimmers, surface-mounted pumps, and oil/water separators). Finally, aboveground recovery is less costly and time-consuming than subsurface recovery.

Although the trench method is a time-saving, economical, and effective alternative to the pump-

ing well method in shallow water table situations, the advantages of trenches diminish as the depth to the water table increases. At a given depth, the total cost of excavating, installing a slurry wall to hold up the sides of a deep trench, adding riprap to cover the bottom, and lining the downgradient wall with an impermeable, gasoline-resistant membrane will exceed the costs and advantages of implementing a pumping well system. The depth at which the advantage shifts from one method to the other is, of course, site specific. It depends on many factors, including the size and thickness of the plume, whether the plume is migrating in more than one direction, soil moisture content, and whether the trench can be maintained without collapsing, not to mention other considerations such as local zoning laws and whether the land available is suitable for trench excavation. Therefore, at sites with shallow water tables, there are no strict rules governing when to implement the different methods. Situations may arise in which the advantages of using one method may offset the advantages of using the other.

Beyond depths of 10 to 15 ft the feasibility of using the trench method is significantly reduced, and at these depths the pumping well method is almost always implemented. Like trenches, pumping wells can be used to contain the migration of the gasoline plume, but unlike trenches, which must be dug across an area large enough to intercept the flow of the plume, a single well installed below the water table can draw in water from all directions and reverse the spread of the gasoline plume. Wells are particularly useful in recovering large spills that have spread over a wide area. By drilling several wells and coordinating their pumping rates, the cones of influence created by the wells can be overlapped to contain the migration of a diffuse plume.

All four trench recovery equipment options (skimmers, filter separators, surface-mounted pumps, and oil/water separators) are equally capable of recovering free product. Similarly, they can each be purchased for an initial capital cost of under $10,000 (with the exception of large oil/water separators).

When considering the overall ease of operation, however, filter separators have several advantages. First of all, they are lightweight, portable, and can float in trenches; second, gasoline is passively (i.e., no energy inputs are required) separated from the trench water with an oleophilic filter; and finally, water does not have to be removed from the trench to facilitate recovery.

The main disadvantage associated with filter separators, though, is that they are only able to reduce a plume's thickness to a sheen on the water surface. The sheen, defined as an iridescent oily film on the water surface, is still considered to be free product. To remove the sheen and the remaining dissolved gasoline constituents, trench water must be pumped out and treated with secondary treatment equipment such as air strippers and activated carbon filters. If the gasoline plume poses an immediate threat to adjacent groundwater sources and rapid recovery is required, single pump and oil/water separating systems offer a distinct advantage: by pumping a steady flow of gasoline and water from the trench, significant recovery of free product and dissolved constituents can be achieved quickly.

The two types of recovery systems most commonly used in pumping wells are the dual pump systems and the single pump and oil/water separator systems. The two are comparable in many respects. Both have high gasoline recovery efficiencies, they are similarly priced in many instances, and both have been successfully employed in numerous recovery operations.

In deciding which system offers the most advantages, the characteristics of the plume and the recovery site must be considered. If, for example, the gasoline spill is at or near a critical groundwater source and rapid recovery is paramount, oil/water separation systems may be advantageous. The two reasons for this are: (1) gasoline and water pumped together in a single pump can be removed faster than if two free-product-only pumps are used; and (2) by generating only shallow cones of depression with single pumps, less soil will be exposed to the gasoline plume. On the other hand, if large volumes of water must be extracted, it may be more economical to use a dual pump system. By recovering free product from within the well itself, the amount of water that must be treated is significantly reduced.

The differences between the two systems are outlined in Table 9 on the following page.

Table 9

Advantages and Disadvantages of Dual Pump Systems vs. Single Pump and Oil/Water Separator Systems

Dual Pump Systems	Single Pump and Oil/Water Separator Systems
Advantages	Advantages
Two pumps recover gasoline and water separately	Requires one pump with no sensor
Pumps only when product is present	Shallow depressions in water tables will minimize additional soil contamination by plume
	Allows more rapid recovery of product
Instantaneous separation of gasoline	Lower operation and maintenance costs
Pumps are portable	Multiple well costs are lower because a single separator can be used for many wells
Disadvantages	Disadvantages
Requires two pumps with sensors	Single pump mixes gasoline and water thus complicating separation
Deep depression in water table may cause further soil contamination by plume	Requires 10- to 12-min detention time for separation
	Pumps continuously (even if product is not present)
High operation and maintenance costs	Separator is stationary
Multiple well costs are high because two pumps are needed for each well	The higher the pumping rate, the larger the separator and the greater the equipment costs

Case Studies

When considering alternative remedial techniques and the costs and advantages of different equipment, it is useful to study solutions that have already been applied to leaks. A review of case histories provides insights into approaching problems and anticipating complications.

Case Study No. 1: 83,000 Gallons

In October 1975, a leak developed in an aboveground storage tank at a defense fuel supply station in Virginia. An estimated 83,000 gal of JP-4 jet fuel was lost. The spill did not pose an immediate threat to drinking or irrigation water supplies, but it was determined that the fuel could migrate off-site and contaminate a spring-fed pond. Different containment options were considered.

The first option involved digging a trench down to the groundwater surface to intercept the free product plume. This idea was abandoned, though, when it was decided that the sandy soil on the site and the depth to the water table (17 ft) would inhibit containment and recovery of the fuel. The soil above the water table was too wet to support a trench.

The second option was to drill a production-type well and use a single pump system to recover both fuel and water for aboveground separation. It was thought that by using one or more wells, the groundwater gradient could be reversed and the free product plume could be contained. This plan was not implemented, however, because a qualified contractor and the necessary equipment could not be located in time.

The third alternative was a "well point system" using two lines of 4-in PVC piping to intercept the flow of the plume. It was thought that by setting the two lines of 25-hole pipes flush with and perpendicular to the flow of the water table, a mixture of plume and water could be skimmed off the surface and the free product would be thus contained. This option was finally selected.

In implementing the well point system, the PVC pipes were connected to a surface-mounted 6-in centrifugal pump. The recovered mixture of fuel and water was pumped into a preexisting dike drainage collection system that led to an oil/water separator. During the first two weeks of pumping, the extraction rate decreased from 650 gal/min to 200 gal/min and the amount of fuel recovered decreased from 1,200 gal/d to 600 gal/d. After an additional two weeks of continuous pumping, the system yielded only 30 gal/min and fuel recovery fell to an average of 380 gal/d. At the end of the fifth week a total of 20,800 gal of fuel had been recovered and the well point system was shut off. Later, a 40-point well system was installed a few feet below the first, but no additional fuel was recovered.

Installation and equipment rental costs for the five weeks was $21,500, and an equal amount was spent on operational and overtime costs. Cost per gallon of recovered fuel was $2.07 overall, with a marginal recovery cost of $3.14/gal at the end of the recovery operation. Of the original 83,000 gal of jet fuel spilled, only 25 percent was recovered. The remaining fuel was assumed to be contained within the interstices of the soil where it would be subject to physical, chemical, and biological degradation. The recovered fuel was mixed and burned with boiler fuel.

Case Study No. 2: 3,000 Gallons

A gasoline storage tank leak in Provincetown, Massachusetts, endangered the town's drinking water supply. The gasoline spill occurred at a service station located 600 ft from the South Hollow well field, which supplied more than 60 percent of Provincetown's drinking water. The 3,000-gal spill contaminated a half-acre area above an aquifer which contributed directly to the well field. Concentrations in excess of 1,000 ppm of gasoline-related hydrocarbons (including benzene) were found in the groundwater. When it was determined that the contaminants were migrating toward the well field, the well field was shut down.

To control the flow of the free product plume, an innovative containment system was devised. The system was composed of two recirculation cells: a smaller cell within a larger one. In the inner cell, four recovery wells were drilled downgradient of the service station to intercept the plume. Single pump recovery systems installed in the wells extracted both water and gasoline from the surface of the aquifer. The recovered gasoline-water mix was then pumped through an oil/water separator to separate the undissolved gasoline emulsions. Next, the separated water was passed through an air stripping tower and activated carbon filters to remove the dissolved hydrocarbon constituents. After being treated, the water was placed in a recharge bed upgradient of the contaminant plume in order to flush trapped gasoline emulsions from the soil and provide a constant flow of water through the cell. The inner cell was designed to circulate 36,000 gal/d. The outer cell, comprising a single production well and recharge chamber, was capable of circulating over 100,000 gal/d and was

installed to provide additional containment in case the plume moved beyond the influence of the inner cell.

In all, 700 gal, or 23 percent of the original gasoline spill, was recovered. The total cost of recovering the free gasoline, including well drilling costs, the oil/water separator, the pumps, and construction and engineering services, was approximately $49,220, or $70.31/gal. These figures were extrapolated from costs for the entire water treatment system and are therefore somewhat higher than the cost of a free product recovery system purchased separately; also, due to the small size of the spill, the economies of scale were poor.

Case Study No. 3: 2,000 to 4,000 Gallons

In 1984, a retail gasoline station in eastern Massachusetts reported a leak of regular leaded gasoline from an underground tank. At the time, the operator drained the tank and discontinued its use, but the other tanks were maintained and the station remained open until 1985. Because the leak occurred at a low rate over a long period of time, it was difficult to estimate how much gasoline was lost. Best estimates are that between 2,000 and 4,000 gal leaked from the tank.

In order to contain the spread of the plume and recover the leaked gasoline, a 6-in diameter recovery well was drilled. A stainless steel, submersible water table depression pump installed in the well removed water at a rate of 75 gal/min or 108,000 gal/d, and a submersible petroleum pump was deployed to recover the gasoline from the water table depression. Water extracted from the well was run through a 3-ft diameter packed air stripping tower to remove dissolved, volatile hydrocarbons. After passing through the air stripping tower, the treated water was discharged into an aquifer recharge trench located upgradient of the recovery well.

The system was installed and activated in March of 1985 and has been in operation since. To date, approximately 1,200 gal of gasoline have been recovered. Since May of 1986, no free floating hydrocarbons have been detected in the wells. At the most recent monitoring (November 11, 1986), the maximum dissolved hydrocarbon level detected was 9.1 ppm.

The total cost to recover the spilled gasoline, including well installation, water table depression and product recovery pump systems, trench excavation, O&M costs, and gasoline disposal costs, was $112,000, or $93/gal of recovered gasoline. It should be noted that in Massachusetts, contaminants recovered from subsurface spills are classified as hazardous wastes and must be disposed of accordingly.

Case Study No. 4: 100,000 Gallons

In May of 1983, a gasoline leak was reported in an underground tank at a service station in North Babylon, New York. An estimated 100,000 gal had been lost. Observation wells installed in the service station property revealed that floating free product was present 11 to 12 ft below the ground surface.

In some places the gasoline plume was found to be as much as 18 in thick. Forty-four observation wells were installed to develop groundwater contours and to determine the direction of groundwater flow. Once the plume was located, surface-mounted product recovery pumps were sent down some of the 4-in observation wells to initiate the cleanup process while an automated system was being devised. In the first week, 750 gal of gasoline was recovered.

To contain the migration of the plume and increase product recovery rates, three 26-in wells were installed. The wells were placed 100 to 200 ft apart in a line parallel to the water gradient. In the upgradient well, which was nearest to the center of the gasoline plume, a 15-hp submersible water table depression pump was deployed. The pump extracted water from below the water table surface at a rate of 300 gal/min. As gasoline accumulated in the well, it was removed with surface-mounted product recovery pumps. The system began operating on July 3, 1983, and within five months 27,000 gal of gasoline had been recovered. Gasoline that had migrated beyond the influence of the upgradient well was recovered in the first downgradient well. The second downgradient well has yet to recover any gasoline. To date (November 1986), 28,500 gal of gasoline has been recovered.

The water being extracted from the wells contains dissolved hydrocarbons, and it therefore requires further treatment with air stripping towers. Air strippers are able to remove from 90 to 95 percent of the dissolved constituents. Once air stripping is complete, the treated water is being discharged to a natural water course, and the recovered gasoline is being re-refined and sold. The total cost of recovery, including the three wells, three dual pump systems, labor, engineering, and O&M costs to date, has been nearly $225,000 ($337,500 if air and water testing and indoor vapor monitoring costs are included). This translates to $7.89 ($11.84) per gallon of gasoline recovered.

Discussion of Case Studies

By comparing the four case studies, an important conclusion can be drawn: the cost of recovering free product at a site depends more on the recovery method and equipment required to perform the cleanup than on the size of the spill. Case No. 3, for example, was a gasoline spill of between 2,000 and 4,000 gal in which $112,000 was invested in recovery operations, while in Case No. 1, 83,000 gal of jet fuel was lost, but only $43,000 was invested in recovery.

The differences in costs result from the different recovery methods used. In Case No. 3, a 48-ft by 6-in well was drilled, and a dual pump system was used. In Case No. 1, a 4-in PVC pipe-interceptor, which acted in much the same way as a trench, was embedded at 17 ft, and an oil/water separator was used for free product recovery. In comparing costs, well drilling is (as a rule) considerably more expensive than PVC pipe installation. Moreover, in Case No. 3, recharge trenches were dug to fuel the recirculation cell, and the recovery equipment was purchased outright by the service station owner in anticipation of a long-term cleanup operation. In Case No. 1, on the other hand, recirculation was not needed and the recovery equipment was rented, not purchased, by the polluter because of the short duration of the cleanup.

It should be noted that, although the renting of recovery equipment is an option in cleanup operations, it may become uneconomical if long-term recovery is required. Also, had recovery equipment been purchased, not rented, the increased costs would still have left the small costs of Case No. 1 far short of those of Case No. 3.

Other examples of cost disparities among the case studies can be seen in Table 10

Cases 2 and 3 also show that free product recovery costs are more dependent on the cleanup method and equipment selected than on the size of the spill. Both cases involved gasoline spills of roughly 3,000 gal, both occurred in sandy-gravel aquifers, and both had relatively deep water tables. Yet, despite these similarities, different recovery systems were implemented in the two cases, and the costs of recovery in Case No. 3 were twice what they were for Case No. 2. The main difference between the two spills was the threat of migration that each posed to adjacent, uncontaminated groundwater sources.

In Case No. 2, the spill was migrating rapidly toward a drinking water well field. As a result, single pumps were sent down four recovery wells, a mixture of gasoline and water was pumped off to an oil/water separator, and in a relatively short period of time, the migration of the gasoline plume was contained.

In Case No. 3, the spill did not endanger other groundwater sources, and the more time-consuming process of establishing and maintaining a cone of depression with a dual pump system was undertaken.

Another important conclusion that can be drawn from the four case studies is that in any given gasoline spill, more than one recovery option may be available. For example, in Case No. 1, two alternatives were considered: (1) to drill a well and use a single pump and an oil/water separator; and (2) to install a PVC pipe interceptor network, a surface-mounted pump, and an oil/water separator. Both choices were viable, but because a qualified contractor and the necessary equipment could not be located in time, the well system was abandoned and the interceptor pipe had to be installed.

As a general rule, the shallower the water table at the site, the greater the number of effective remedial techniques available. This is especially true of sites where the water table is less than 15 ft from the ground surface, in which case the trench method, the dual pump method, or the single pump and oil/water separator method may be used.

One final point that should be made regarding the case studies is that although recovery costs may vary from site to site, these costs are relatively small when compared with the total cost of restoring gasoline-contaminated groundwater to drinking water standards. Removing dissolved gasoline constituents with air strippers and activated carbon filters is often so costly that any savings achieved by economizing on free product recovery strategies are insignificant.

Table 10
Cost Summary for Case Studies

Case No	Spill Size gal	Duration of Recovery	Amount Recovered gal	Total Cost	Cost/gal Recovered
1	83,000	5 wk	20,800	$ 43,000	$ 2.07
2	3,000		700	49,220	70.31
3	2,000-4,000	15 mo	1,200	112,000	93.00
4	100,000	7 mo	28,500	225,000	7.89

Section 4

Gasoline Removal From
Soils Above the Water Table

This section provides an overview of corrective action technologies for removing gasoline from unsaturated soils. The discussions cover the basic mechanisms of removal, the effectiveness of the corrective action under different situations, and potential limitations of the technology. Also included are estimated ranges of costs for implementation of the alternatives.

A number of regulatory issues are associated with the cleanup of contaminated soil. These regulatory issues include determinations of what is considered a contaminated soil, how those determinations are made, and how and where contaminated soils shall be disposed of. It is not the intent of this section to focus on and resolve these issues; rather, this section provides useful information on the cost and effectiveness of soil treatment alternatives.

The corrective actions for gasoline-contaminated soils discussed in this section include:

• Excavation and disposal. Contaminated soil is dug up and sent to a landfill.

• Enhanced volatilization. Rototillers and other mechanical devices are used to increase the evaporation of volatiles.

• Incineration. Contaminated soils are burned at high temperature.

• Venting. Gasoline vapors are removed from the soil without excavation.

• Soil washing. Gasoline constituents are leached from the soil matrix.

• Biodegradation. Bacteria degrade gasoline either in situ or aboveground in reactors.

Much information has been gathered on various soil treatment techniques, but a great deal of uncertainty remains about how the techniques work, and what the controlling factors are to achieve maximum effectiveness. Soil treatment has not been used as widely as groundwater treatment such as air stripping and carbon adsorption. A large body of engineering information exists for groundwater treatment technologies; they are widely understood, the theories and related equations have been thoroughly developed, and the principal design parameters are well known. This is not the case for soil treatment, however, where the technologies are not well understood or well developed. The information contained in this section for many of the soil treatment technologies is based on research results and preliminary pilot studies.

Excavation and Disposal

Gasoline-contaminated soil may be excavated and transported to an approved disposal facility with conventional construction equipment. It is probably the most widely used corrective action undertaken for gasoline-contaminated soils at this time; however, the increasing costs and ultimate disposal problem of this alternative will make it less attractive in the future. The EPA (1984) provides detailed descriptions of soil excavation and transport systems for remedial actions at uncontrolled hazardous waste sites. The equipment types generally used for excavation of soil include backhoes, cranes, dozers, and loaders, and they would be expected to be used for removing leaking underground storage tanks (USTs) and piping.

Effectiveness

Excavating contaminated soils as an adjunct to tank removal may be an appropriate way to eliminate the major source of continued gasoline migration to the subsurface environment. Product will drain from a soil saturated with gasoline under the force of gravity until residual saturation is reached. At residual saturation no additional fluid migration from the soil should occur unless precipitation washes gasoline from the soil profile.

The characteristics of a soil largely determine its capacity to retain gasoline in liquid and gaseous

phases under unsaturated conditions. Excavation of soils at residual saturation can effectively remove product from the environment. As shown in Table 11, excavating dry, fine-textured sands would be more effective than coarser textured sands or those that are at field capacity, because coarser sands retain less gasoline.

Hoag and Marley (1986) evaluated the residual saturation of gasoline in soil columns filled with coarse sand, medium sand, fine sand, or a mixture of coarse, medium and fine sand. The residual saturation of the sands was evaluated under dry conditions at field capacity as well as three different column-packing densities. Table 11 lists the degree of saturation by gasoline of the soils determined by Hoag and Marley (1986), expressed as the ratio of the volume of gasoline to the volume of pore space. They determined that gasoline residual saturation decreases with increasing particle diameter, and that a soil's capacity to retain gasoline decreases when soils are at field capacity as compared to dry soils. They also determined that at increased densities the soil is able to retain more gasoline because of the increase in total available surface area per unit volume and the attendant decrease in the average soil pore diameter.

Corrective actions that remove soils saturated with gasoline would be expected to minimize effectively the further migration of gasoline from the soils to the water table. Soils at residual saturation would not be expected to release substantial quantities of product provided percolating precipitation or a fluctuating water table is not a factor.

Limitations

Although gasoline-contaminated soils can be excavated with conventional construction equipment, the depth at which these implements can remove soils is limited. Backhoes with 0.5 yd^3 of capacity have a maximum reach of 26 ft and a maximum excavation depth of 16 ft. Larger backhoes (e.g., 3.5 yd^3 capacity) have the ability to remove soils at depths of up to 45 ft at maximum digging angles of 45° (EPA, 1984). Because of the shallow angle of repose expected to be encountered in most situations, a significant amount of surface area will be disturbed relative to the depth excavated.

Leaking USTS are found in various settings. Those under paved areas, under buildings, or where substantial underground or overhead utilities exist may not be as amenable to excavation as those where little pavement or few structures exist. Congested or heavily traveled areas may also limit excavation techniques as a means of corrective action. Excavation operations which interfere with the business may be in some instances an unacceptable alternative.

Excavation requires the contaminated soils to be removed to a considerable depth and then placed on the soil surface or into transport vehicles. The nature of excavation increases the potential of exposing workers and the public in general to the contaminants. For example, the removed soil is susceptible to the effects of rainfall, which could lead to runoff of contaminated materials from the site. Therefore excavation facilities should be

Table 11
Gasoline Retention at Residual Saturation

Sand Type	Moisture Status	Residual Saturation	
		Percent	g/kg
Fine	Dry	54 - 60	92 - 122
	Field capacity	20 - 26	34 - 44
Medium	Dry	15 - 27	35 - 47
	Field capacity	13 - 18	24 - 37
Coarse	Dry	15 - 19	34 - 44
	Field capacity	— —	— —
Mixed	Dry	46 - 60	55 - 68
	Field capacity	— —	— —

Source: Adapted from Hoag and Marley (1986)

designed and operated to adequately protect the health and safety of workers and the public, as well as the environment.

The void created as a result of excavation must generally be filled with clean soil as part of the corrective action. The clean soil, however, can be contaminated by the fluctuation of water table elevations containing gasoline components. Therefore, excavation may be most appropriate in situations where soils are contaminated with gasoline components above the residual saturation level.

In general, excavation may be an effective means for removing contaminants from the soil environment; however, for the overall corrective action to be effective, there must be a suitable means of disposal.

Pursuant to RCRA and the Hazardous and Solid Waste Amendments of 1984 (HSWA), EPA promulgated Land Disposal Restrictions (40 CFR 268) on November 7, 1986 (FR 51(216):40572-40654). Effective November 8, 1986, certain solvent- and dioxin-contaminated soils are prohibited from land disposal unless they result from CERCLA or RCRA response actions. Soils resulting from CERCLA and RCRA response action are excluded from prohibition through November 8, 1988.

Soils prohibited from land disposal include those containing dioxin and those contaminated with F001-F005 solvent constituents at concentrations greater than 1 percent. The F001-F005 solvents include components typically encountered in gasoline, such as ethylbenzene, toluene, and xylene. Gasoline products typically contain approximately 2 percent ethylbenzene, 12 percent toluene, and 8 percent xylene by weight. Therefore, it is likely that soils saturated with gasoline could exceed the 1 percent limit for solvents and thus be subject to land disposal restrictions.

Land disposal appears to be the most common method for disposal of gasoline-contaminated soils even though the potential liability associated with it poses severe limitations. Since gasoline is amenable to thermal destruction, volatilization, and biodegradation, it may be best to opt for such treatment rather than land disposal.

Costs

Costs for excavation and disposal can be segregated into the following components: site preparation, excavation, material handling/staging, backfill material, final grading, hauling, and disposal.

Site preparation costs may be minimal where only minor excavation is required but may be significant when large areas must be cleared. Site clearing costs can range from $1,500 to $2,300/acre when grubbing and stump removal is required. Where paved areas are to be excavated, site preparation costs may not be incurred.

Excavation costs will vary depending on the type of equipment used. Backhoes/front end loaders with capacities of 0.5 to 0.75 yd^3 range from $3.55 to $5.00/yd^3$ (Means, 1987); backhoes with 1 to 3.5 yd^3 capacity range from $1.75 to $3.00/yd^3$ (EPA, 1984).

Material handling/staging costs range from $1.20 to $4.50/yd^3$ depending on unit costs for dozers and loaders moving soils on site.

Backfill material will cost from $10 to $20/yd^3$ depending on the distance the material is hauled.

Grading at the backfill will add an additional $2.50 to $3.50/yd^3$ to the costs of the backfill placement.

Hauling costs for removal of the soil to the disposal site are largely dependent on the distance traveled but range from $0.50 yd^3/mi to $1.00 yd^3/mi.

Disposal costs are highly affected by the type of waste. Landfill tipping fees for ignitable wastes are estimated to be $120/ton and for toxic wastes, $240/ton (EPA, 1974). Landfill disposal, including transport, of gasoline-contaminated soils typically ranges from $125 to $200/yd^3$ according to a number of corrective action contractors. Tipping fees as low as $5/yd^3$ were reported for "clean soils" and as high as $120/yd^3$ at licensed hazardous waste facilities. The majority of landfills reportedly require flash point analysis at a minimum, with soils having flash points below 140°F being rejected. One tank installer indicated that flash point is the characteristic that most often causes soils to be rejected for disposal by a landfill. This contractor has found that spreading contaminated soil out on plastic sheets and allowing volatilization to occur renders the soil "clean" enough for disposal in a municipal landfill at a tipping fee of $5/yd^3$. In this type of operation, soil disposal costs may be as low as $40/yd^3$ including excavation and hauling.

A significant amount of gasoline-contaminated soil is apparently also being disposed at batch asphalt plants. These facilities utilize the contaminated soils in their production process. One plant charges $55/yd^3$ for disposal provided the soil has passed the EP toxicity test and does not contain chlorinated solvents. (EP refers to an extraction procedure, one test of several to determine whether or not a solid waste is a hazardous waste under RCRA.) States differ with regard to control of asphalt plant operations. In Massachusetts, for instance, asphalt plants do not accept gasoline-contaminated soils because they would then be subject to the hazardous waste regulations applicable to transport, storage, processing, and disposal

facilities. Rhode Island, on the other hand, apparently has no such requirement; asphalt plants will accept gasoline-contaminated soils provided they do not contain chlorinated solvents.

Enhanced Volatilization

Enhanced volatilization is any technique that removes volatile organics from unsaturated soil by putting contaminated soils in contact with clean air in order to transfer the contaminants from the soil into the air stream. The air stream is further treated through the use of carbon canisters and/or water scrubbers or afterburners to reduce air emission impacts. A number of different methods are available that can achieve this effect: mechanical rototilling, enclosed mechanical aeration systems, low temperature thermal stripping systems, and pneumatic conveyer systems.

● Mechanical Rototilling

This method involves turning over soils to a depth of about 1 ft below the surface to increase the rate of volatilization. Several passes of the rototilling equipment over the soil may be required to effect sufficient volatilization. Following treatment, the topsoil is moved to a nearby pile, and rototilling is performed on the next 1 ft of soil. The effectiveness of this method is highly dependent on weather conditions. High speed rototillers and soil shredders can enhance the rate of volatilization.

● Enclosed Mechanical Aeration Systems

To effect volatilization, contaminated soils are mixed in a pug mill or rotary drum. The gasoline components are released from the soil matrix by the churning action of air/soil contact. The induced airflow within the chamber captures the gasoline emissions and passes them through an air pollution control device (e.g., water scrubber or vapor-phase carbon adsorption system) before they are discharged through a properly sized stack.

● Low Temperature Thermal Stripping Systems

This configuration is similar to the enclosed mechanical aeration system except that additional heat transfer surfaces allow the soil to heat by coming into contact with a screw-auger device or rotary drum system. The induced airflow conveys the desorbed volatile organics/air mixture through a combination afterburner where organic contaminants are destroyed. The air stream is then discharged through a properly sized stack.

● Pneumatic Conveyer Systems

These systems consist of a long tube or duct to carry air at high velocities, an induced draft fan to propel the air, a suitable feeder for addition and dispersion of particulate solids into the air stream, and a cyclone collector or other separation equipment

for final recovery of the solids from the gas stream. Several such units heat the inlet air to 300°F to induce volatilization of organic contaminants. Pneumatic conveyers are primarily used in the manufacturing industry for drying solids with up to 90 percent initial moisture content.

Of the four methods described above, documentation exists to support the contention that low temperature thermal stripping systems have the greatest ability to successfully remove contaminants that are similar to gasoline constituents (i.e., compounds with high vapor pressures) from soil.

Roy F. Weston Inc. (1986) conducted studies using a pilot system comprised of several conveyer belts, a heated screw auger conveyer, and storage hoppers along with primary process equipment. The heart of the treatment system is the thermal processor which heats the soils sufficiently to volatilize the organics. Once volatilized, the organics are destroyed in an afterburner. An indirect heat transfer fluid, in this case oil, is used to heat the thermal processor, and the soil is conveyed from the feed end of the thermal processor to the discharge end by twin screws. Hot oil (ranging from 100-300°C) travels the full length of each screw, then returns through the center of each shaft continuously throughout system operation (Figure 8). The continuous movement of the screws conveys and thoroughly mixes the contaminated soils. The soils have a residence time of 30 to 60 min in the screw auger-type dryer. The exhausted air stream passes through an afterburner at a temperature of 1000°C to destroy organics.
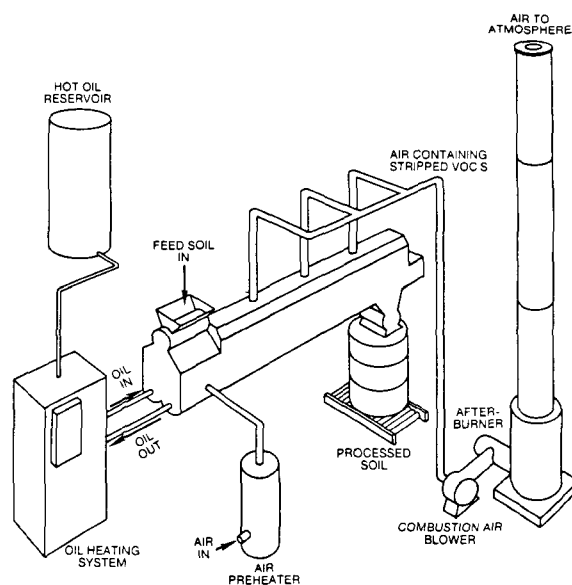

Figure 8. Low temperature thermal stripping pilot system.

A low temperature thermal stripping system was used to remove trichloroethylene (TCE) from soil during a full-scale pilot study conducted by Canonie Environmental Services Corporation at the McKin Superfund Site in Gray, Maine (Webster, 1986). Although the principal volatile of concern was TCE, the system also effectively reduced benzene levels to less than 1 ppm, or 1 mg/L (see Effectiveness, this page). The system involved conveyer belts, a large rotating drum-type materials dryer and storage hoppers, in addition to primary process equipment. Excavated soil was fed into the drum and mixed at 300°F. Exhaust air from the enclosed aeration process was treated in a baghouse, a scrubber, and a vapor-phase carbon bed prior to release.

The materials dryer used for soil aeration in this pilot study was an asphalt batch plant to remove moisture from fine and coarse aggregates. The dryer was a large, rotating cylindrical drum approximately 9 ft in diameter and 28 ft in length. Pre-aerated, contaminated soils were introduced to the dryer by conveyer belt and fed by a front-end loader and hopper. Forced hot air was generated by an oil burner and introduced to the drum to enhance vaporization of volatile organic compounds (VOCs). During aeration runs, the drying temperature varied from 150 to 330°F. The exhaust air from the materials dryer was treated in a three-stage process to remove particulates and organic vapors. The first stage of air pollution control utilized a baghouse normally used with the asphalt batch plant. Exhausted air from the baghouse was conveyed via ducts to the packed tower air scrubber, the second phase of air pollution control. The dryer retention time was 6 to 8 min, with a typical soil volume of approximately 3 yd^3 passing through the dryer a minimum of three times. The scrubber was used to condition the air prior to vapor-phase carbon adsorption and to remove water-soluble chemical constituents and remaining particulates. In the final stage of air pollution control, a vapor-phase carbon adsorption bed was used to remove VOCs.

The system used during a full-scale pilot study conducted at a Superfund site in Region IV was somewhat similar to the system described for the McKin pilot study with the exception of having less stringent air quality control equipment. It included an asphalt drying unit, an asphalt preheater, conveyer belts, and a particulate collection system. In this system, soil was gravity fed through a rotating preheater, and fuel was burned at the opposite end of the system. Organics were vaporized from the soil through agitation of the rotating preheater and exposure of soil to gas at 375°F at a feedrate of 10 to 15 tons/h. Particulate emissions from the treatment unit were collected in a cyclone and a cloth baghouse. Some volatile material emissions were discharged into the surrounding atmosphere.

Effectiveness

The three full-scale pilot studies described above demonstrated greater than 99.99 percent removal of VOCs based on a review of post-aeration soil sampling data. Based on a review of air monitoring organic emissions data, it can be concluded that none of the treatment systems jeopardized public health or the environment.

The McKin pilot study (Webster, 1986) was undertaken to determine optimum operating conditions to produce a consistent, post-aeration soil TCE concentration less than the 0.1 ppm target level established by EPA. The sandy soils treated were contaminated with up to 3,310 ppm TCE. To allow for evaluation of such operating parameters as dryer temperature, dryer airflow, soil volume per run, number of passes through dryer, total dryer retention time, dust control, and handling of collected baghouse particles, the study was conducted in four phases. The optimal operating conditions determined in the four phases are presented in Table 12.

The results suggest that for highly contaminated soils, dryer temperature is a significant factor in meeting treatment objectives, with higher temperatures yielding lower post-aeration TCE concentrations. Control of the dryer airflow is also an important operating parameter because of its effect on air temperature. Maintaining consistent treatment efficiencies and baghouse temperatures to protect the synthetic filters was difficult with low airflows.

Although the primary compound of concern in the McKin soil aeration pilot study was TCE, the results suggest that the aeration process was also effective in removing other volatile organic compounds from soils. Tetrachloroethylene and 1,1,1-trichloroethane detected in 1- to 100-ppm ranges in pre-operation samples were routinely not detected above 1 ppm in post-aeration samples. The efficiency of removing aromatic volatiles such as benzene was also examined. Among the excavated soil samples, two had 680 ppm and 2,600 ppm of benzene, the highest concentrations by several orders of magnitude.

In post-aeration analyses of these soil batches, benzene was not detected at a 1.0 ppm detection limit. Similar significant decreases were found for other aromatic volatiles such as ethylbenzene, toluene, and xylenes. In addition, the pilot study showed that controlled soil-handling techniques and treatment of the process air contributed only negligibly to air quality impacts due to organic vapors. To reduce dust emissions from the opera-

Table 12
Optimal Operation Conditions for McKin Pilot Study Configuration

Parameter	Optimal Condition
Dryer temperature	300°F
Dryer air flow	15,000 cfm
Dust control	Enclosed bucket conveyer system, wetting soil only after final pass through dryer
Handling of collected baghouse particulates	Treated separately in enclosed, heated conveyor
Soil volume per run	3 yd³
Number of passes through dryer	Minimum of three
Total dryer retention time	6 to 8 min

Source: Webster, 1986.

tion, enclosed handling of treated soils proved necessary.

The pilot study conducted at a Superfund site in Region IV (1986) demonstrated that the treatment unit was able to effectively treat 1,670 tons of contaminated soil by reducing the concentration of volatile organics present. Concentrations of 1,1,1-trichloroethene, TCE, toluene, and xylene were reduced by at least 99 percent. For example, sandy soil TCE concentrations of 20 ppm were reduced to 0.055 ppm following thermal treatment, and soil ethylbenzene concentrations of 10 ppm were reduced to 0.018 ppm following treatment.

Limitations

The limitations of low temperature thermal stripping systems as an enhanced volatilization technique are associated with soil characteristics that inhibit the mobility of gasoline vapors from the soil to the air, contaminant concentrations that may cause an explosion or fire, and the need to control air quality impacts due to dust and organic vapor emissions.

Costs

Rototilling or other mechanical means would not be considered a potentially appropriate corrective action unless the contaminated soil could be spread over a large area and treated for extended periods of time. This type of corrective action may be appropriate at sites that are close to existing land treatment facilities or that have substantial acreage on which land farming could be undertaken. In most cases, however, it is expected that corrective actions at UST facilities may be more appropriately addressed by low temperature thermal stripping.

Roy F. Weston, Inc. (1986), under contract to USATHAMA, performed an economic evaluation of low-temperature thermal stripping of volatile organics from contaminated soils in the following categories: 1,000 tons; 10,000 tons; and 100,000 tons. The results of the economic analysis for the four Holo-Flute systems evaluated are presented in Figure 9. Based upon evaluation, it was concluded that System B was the most cost-effective approach for sites with 15,000 to 80,000 tons of soils to be treated. The unit costs for this system ranged from $74 to $160/ton ($99 to $213/yd³) without flue gas scrubbing and from $87 to $184/ton ($116 to $245/yd³) with flue gas scrubbing. Operating costs for stripping 1,000 tons of soil ranged from $42 to $89/ton ($56 to $119/yd³) for the four systems shown in Figure 9. However, the capital costs for the systems are a significant portion of the total costs for processing, as Figure 10 illustrates. Using this type of system, actual costs for processing less than 10,000 tons of soil would be expected to be in excess of $200/ton ($270/yd³). Estimates for thermal stripping of soils using asphalt batch plants may also range upwards of $300/yd³.

SYSTEM A -ONE THERMAL PROCESSOR WITH
TWO 24 INCH DIAMETER AND TWO
24 FOOT LONG HOLO-FLUTE® SCREWS

SYSTEM B - ONE THERMAL PROCESSOR WITH FOUR
24 INCH DIAMETER AND FOUR 24 FOOT
LONG HOLO-FLUTE® SCREWS

SYSTEM C -TWO SYSTEM B UNITS ARRANGED
IN SERIES

SYSTEM D -FOUR PROCESSORS CONSISTING OF
TWO PARALLEL SYSTEM C UNITS

ALL WITH FLUE GAS SCRUBBING
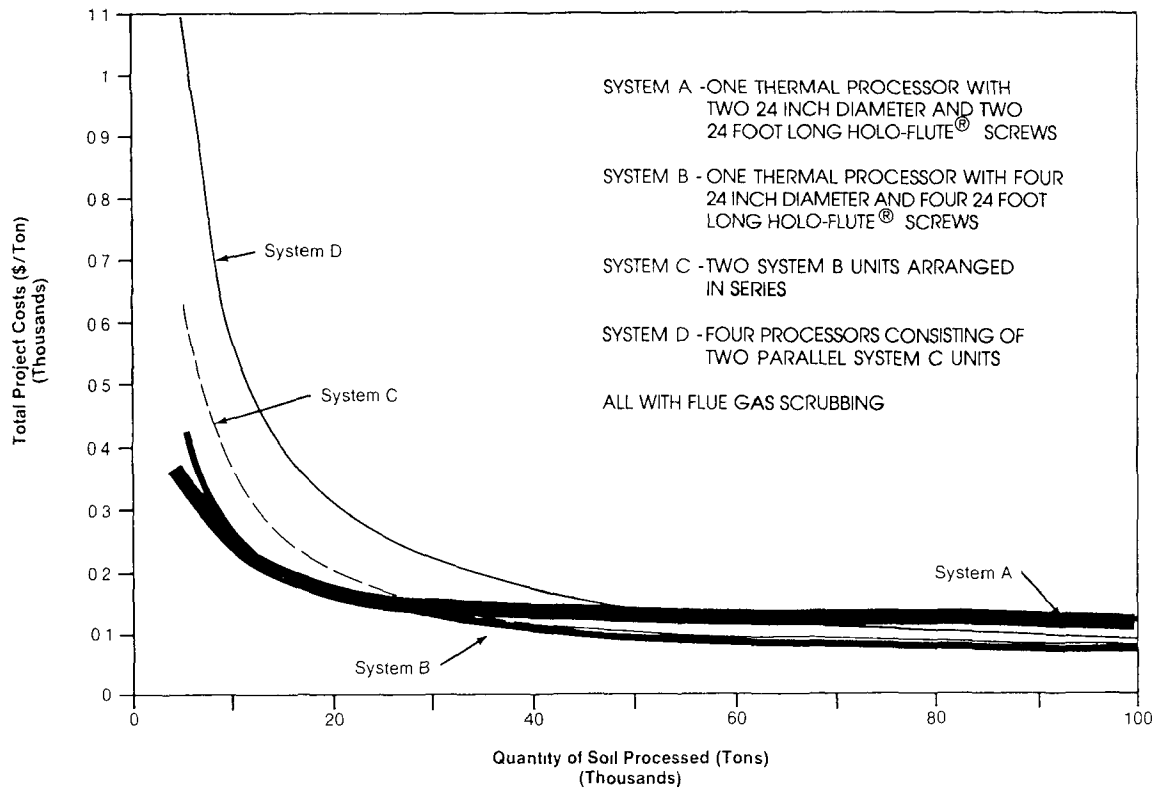
Figure 9. Costs of low temperature thermal stripping pilot plant unit.

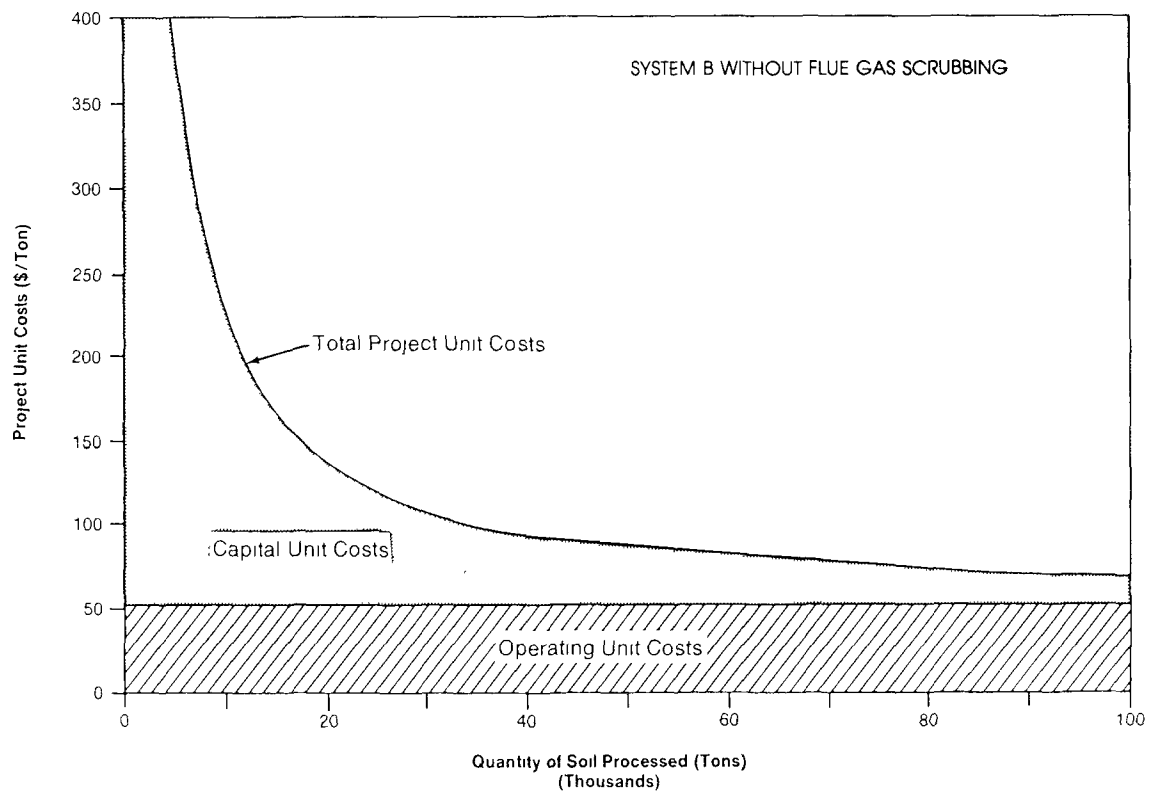SYSTEM B WITHOUT FLUE GAS SCRUBBING

Figure 10. Costs of low temperature thermal stripping unit.

41

Incineration

Incineration can effectively eliminate gasoline from soils by complete oxidation. Rotary kiln and fluidized beds as well as other systems may achieve destruction and removal efficiencies (DRE) of 99.99 percent or greater as required by RCRA for hazardous wastes. Incinerators may be either fixed facility types or mobile units.

Although incinerators may effectively remove gasoline from soils, the same limitations as are associated with soil excavation would be encountered. Use of mobile units is further limited by the permitting process, which may take considerable time and is expensive.

Costs for incineration vary significantly depending on the particular characteristics of the soil and waste material. CDM (1986) conducted a survey of mobile treatment technology vendors and obtained price estimates ranging from $150 to $480/ton ($200 to $640/yd^3) for incineration of 20,000 yd^3 of hypothetical hazardous waste. Unit costs for less than 20,000 yd^3 of material would be anticipated to be significantly greater than those reported.

Venting

Soil venting refers to any technique that removes gasoline vapors from unsaturated soil without excavation. It is accomplished in situ by using vents of various designs (Figure 11) consisting of gravel packs extending to the soil surface, slotted or unslotted well casings installed with or without a gravel pack, or any other configuration that allows gases to move from the soil. Passive systems consist of vents that are open to the atmosphere and do not require energy for extraction of gases. Use of a wind-driven turbine on a vent stack is considered a passive system. Active systems make use of pressure or vacuum pumps to accelerate the removal of gasoline vapors from the soil. In pressurized venting, air is forced into the soil by an infiltrating vent. In vacuum venting, a vacuum created on the extraction well removes vapors. Pressure and vacuum systems could be used in tandem to increase the rate at which gasoline is removed from soils.

With venting, the vapors are either discharged to the atmosphere or treated before discharge depending on vapor concentrations and regulatory requirements.
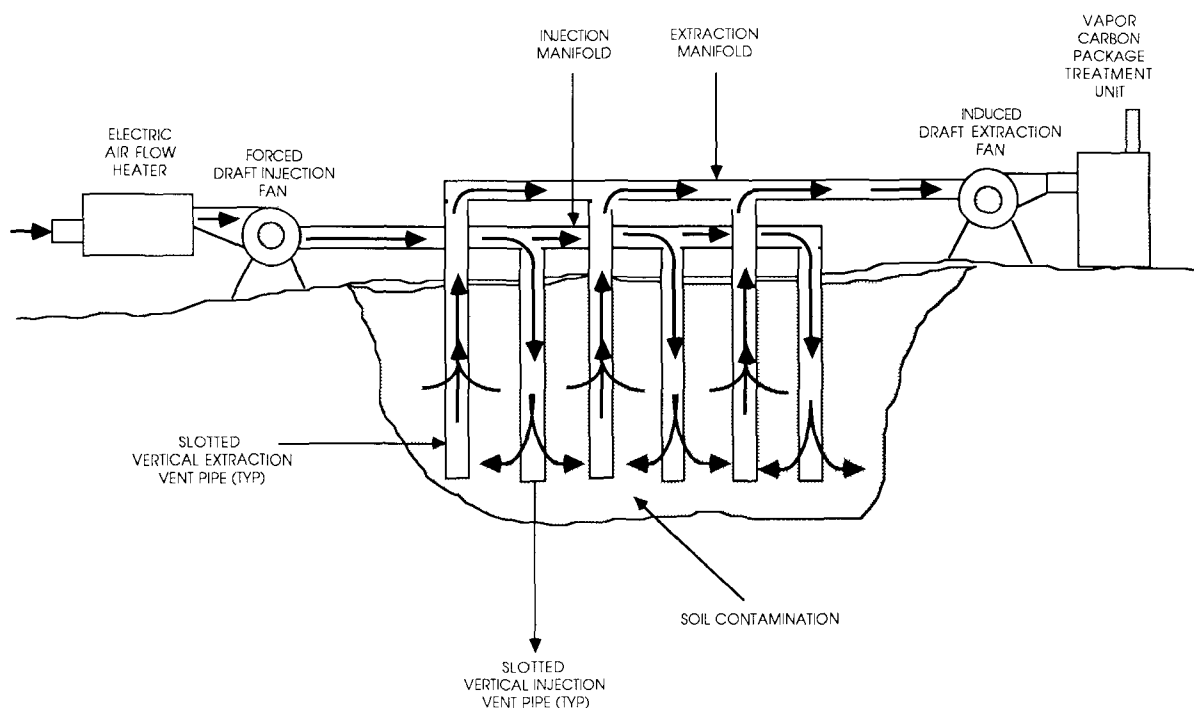

Figure 11. Vacuum extraction system.

Effectiveness

There is much uncertainty regarding the effectiveness of soil venting systems because the technology has not been widely applied. In order to predict the effectiveness of soil venting, several researchers have attempted to develop theoretical models of vapor movement in soil. Hoag et al. (1986) undertook studies to examine the mechanisms and kinetics that control venting of soil residually saturated with gasoline. By using an experimental vessel, they developed a saturated vapor-phase equilibrium model to predict theoretical hydrocarbon mass loss. The experimental data showed good agreement with the predicted values.

However, it is questionable whether this model could be applied to field situations because of the difficulties involved in determining initial values for key variables in the equations. For example, in order to use the equations, the vapor-phase concentration in the soil pores must be determined. Because of the constant flux of soil air, it may be difficult to estimate an initial vapor-phase concentration for gasoline in soil under field conditions.

In addition, the model presupposed that soil particle size, density, and moisture had no effect on the mechanisms involved in the venting process. Although this may have been the situation in the experiment, it is questionable whether the model could be applied to field conditions, where soil characteristics would be expected to significantly affect the rate at which gasoline vapors could be vented from the soil.

The experimental results of Hoag et al. (1986) do indicate, however, that more than 99 percent of gasoline initially present at residual saturation in sands could, theoretically, be removed by soil venting under ideal conditions.

Baehr and Hoag (1986) developed a mathematical model to derive an equilibrium approximation for gasoline present as a solute in the water phase, as a vapor in the air phase, or as a constituent in the immiscible phase. The model was adapted to describe conditions encountered in experimental column tests with one-dimensional flow. The soils in the column had an average particle diameter of 0.89 mm and a porosity of 0.429. The residual gasoline content of the column at the start of the experiment was 0.077, and the experiment was run at an air-phase specific discharge of 1.88 cm/s. The model predictions generally compared very well with the experimental data and provided information leading to these conclusions:

- Removal rates decrease with time during venting as the immiscible phase composition shifts towards a mixture comprised of less volatile com-

pounds corresponding to a lower total vapor pressure of the gasoline.

- Rates at which vapors escape from residual saturations are faster than the maximum rate at which they can be swept from soil above the water table.

- Depression of the water table would result in an increased rate of removal of vapor-phase components due to the removal of the rate-limiting diffusion barrier that results from water in the soil pores within the capillary fringe.

Although the model shows promise for use in designing soil venting installations and for predicting performance of alternative designs, Baehr and Hoag state that additional research and field testing are required before a computer code of practical value can be developed.

The Texas Research Institute, Inc. (1984) undertook a series of four experiments to examine forced venting of gasoline-contaminated soil. These experiments examined the efficiency of removing gasoline from the underground environment and lowering gasoline vapor concentrations in the unsaturated soil under various venting system geometrics and flow rates. Results indicated that venting is an applicable technique for removing gasoline vapors in soils. The reduction in gasoline vapor concentrations in the unsaturated zones were on the order of at least 100-fold at flow rates of 4 L/min or above. Concentrations of gasoline vapor were reduced to 1,000 ppm or less when flow rates of 4 L/min or greater were used. These findings lead to the following general recommendations regarding soil venting techniques for gasoline removal from unsaturated soils:

- Using short slotted sections at the bottom of the import vents may provide more efficient vapor removal than continuous slot vents.

- Sealing the soil surface of the venting area may optimize venting by helping to ensure that exhaust air is drawn laterally, not downward from the soil surface.

- Initiating venting at high flow rates (16 L/min or higher) would remove the majority of vapors, subsequently reducing the flow rate to conserve energy.

Malot and Wood (1985) advocate soil venting before removing free product. The advantage of this approach is that it minimizes the amount of groundwater extracted and treated. Employing product recovery systems which depress the water table results in additional soil volume becoming contaminated as the floating product moves downward with the water table in response to pumping. Although it can be argued that free product removal

activities could in certain instances disperse the contaminants beyond that which would occur if venting systems alone were employed, the benefits of implementing a free product recovery system as the initial corrective action are substantial enough to justify such an approach in most instances.

Malot and Wood (1985) applied a soil venting system at a site where 15,000 gal of carbon tetrachloride was spilled in an area where the top of the unconfined Karst aquifer was 300 ft below ground surface. It was estimated that 4.4 million cubic yards of unsaturated soil materials consisting of clayey silts and silty clays were contaminated. Soil venting systems consisting of slotted screens installed at depths of 75 to 180 ft were used at a vacuum of 29.9 in. Hg and a flow rate of 240 ft³/min. After 90 days the vacuum stabilized within a radius of influence in the soil of 10 ft.

Hoag and Cliff (1985) reported on an actual application of soil venting for remediation of a site where approximately 400 to 500 gal of gasoline had been spilled. Of this total, approximately 80 gal was recovered as free product before soil venting was initiated. The groundwater table was approximately 18 ft beneath this site, and the total aerial extent of the contaminant plume (to 1 mg/L) was 12,000 ft².

Within the contaminated area, three soil vents made of 6-in diameter PVC pipe were installed and connected to 21 ft³/min vacuum pumps. Over the 90-day period of operation, 364 gal of gasoline was recovered; 90 percent of this volume was removed in the first 40 days. After the initial 40 days of operation, only a skim of gasoline remained on the surface of the groundwater table; after 90 days no detectable layer of gasoline was observed in the monitoring wells. The gasoline level in the soil was reduced to levels ranging between 0.5 to 0.1 mg/L over much of the area originally contaminated. The soil venting system employed was effective in removing large volumes of gasoline from the residually saturated soils and from the top of the capillary zone.

Using test cells Crow et al. (1985) investigated hydrocarbon venting at a petroleum fuels marketing terminal. Their studies demonstrated the effectiveness of soil venting at removing gasoline vapors from unsaturated soil and also the potential for using soil venting to remove spilled hydrocarbons from a shallow aquifer. The tests were run using 2-in diameter slotted well casing installed to 20-ft depths in 4-in diameter bore holes backfilled with pea gravel over the 14- to 20-ft slotted depth. Liquid ring vacuum pumps were used to extract vapors at rates ranging from 18.5 to 39.8 ft³/min, and the effective radius of influence extended from each extraction well approximately 50 to 110 ft in the low- and high-rate experiments, respectively.

Payne et al. (1986) reported on the use of a closed-loop forced air circulation system to remove tetrachloroethylene from unsaturated soils at a site in Michigan. Tetrachloroethylene, or PERC as it is commonly called, is a degreaser solvent with a relatively high vapor pressure. Approximately 1,000 to 2,000 yd³ of fine sandy soil was contaminated with PERC at concentrations ranging from 8.3 to 5,600 mg/kg. Soil venting was accomplished with a 2-in diameter galvanized casing withdrawal well installed to a depth of 17 ft in the center of the contaminated area. Five air injection wells were constructed at a radius 50 ft from the withdrawal well, and a sixth was installed 70 ft away. The injection wells consisted of 1.25-in diameter PVC casing extending to a depth of 19 ft. The 5-in diameter borehole for the injection wells was gravel-packed from 19 to 25 ft and in the withdrawal well from 17 to 25 ft.

Air extracted from the withdrawal well was passed through a 96 ft³ filtration bed charged with 1,200 lb of granulated active carbon (GAC). Vacuum levels of 4.5 in. Hg were reached using a 1-hp oilless rotary vane vacuum pump initially. Gaseous levels of PERC reached 92,000 mg/m³ at 48 h declining to 6,000 mg/m³ at 72 h. The PERC levels remained at 5,000 mg/m³ through day 12 and declined to 1,000 mg/m³ on day 19 and to 10 mg/m³ on day 35. After 45 days of pumping, split spoon samples collected contained 0.84 and 0.64 mg/kg. PERC has characteristics similar to BTX components, including high Henry's law constants and similar vapor pressure characteristics. Therefore, it is anticipated that gasoline would respond to venting in a manner comparable to that experienced with PERC.

Anastos et al. (1986) reported on a pilot demonstration of soil venting at a site contaminated with TCE. The pilot tests were run in one area where soil TCE levels ranged from 5 to 50 mg/kg and in another area with levels of 50 to 5,000 mg/kg of TCE. The pilot tests were undertaken to demonstrate the feasibility of soil venting and to allow for the development of design data for a full-scale soil venting system. The pilot system consisted of a series of perforated PVC pipe vents 3-in. in diameter installed vertically into the contaminated soil, through which volatiles were removed, and another series of PVC pipes installed in the soil, into which air was pumped under pressure. The pilot system also included space heaters to heat air used in the system to a constant temperature and a vapor-phase activated carbon unit to treat the exhaust air.

The extraction pipes were spaced 20 ft apart in the area where soil TCE concentrations were 5 to 50 mg/kg, and 50 ft apart in the area of TCE concentrations of 50 to 5,000 mg/kg. Airflow rates of 50 ft³/min and 50 to 225 ft³/min, respectively, were applied.

The exhaust gases from the system were measured with a gas chromatograph/photoionization device (GC/PID) and found to decrease over the 3-month period of the study from an initial value of 5 to 12 ppm in the soil area contaminated with 5 to 50 mg/kg TCE to 500 to 800 ppb. In the highly contaminated soil area, the TCE content in the exhaust gases remained at 250 to 350 ppm over the 3-month project duration. The conclusion was that TCE removal to exhaust-gas levels below 100 ppb might have been achieved through continued system operation beyond the 3-month test period. Because of the chemical similarities between TCE and BTX, comparable removal efficiencies for BTX could likely be achieved.

Limitations

The limitations of venting are associated with soil characteristics that impede free movement of vapors to the extraction well, emissions of volatiles, and explosion hazards.

Soils with limited pore space due to compacted conditions or fine-grained texture could restrict the rate at which air moves through the soil and also the ability of the air to pass effectively over all contaminated soil particles. These types of conditions would require the use of more closely spaced venting wells and possibly higher capacity pumps. Where air quality restrictions apply, volatiles generated during the venting process can be readily captured with GAC. Also, soil bed filters could be used to scrub vented vapors.

Soil bed filters or biofilters have been used extensively for the treatment of malodorous gases associated with wastewater treatment plants (Terasawa et al., 1986). These systems use a soil's chemical, physical, and microbial characteristics to filter odors from gases.

Prokop and Bohn (1985) reported on the use of a soil bed filter for the removal of VOCs including propane and isobutane. This technology could potentially be used with soil venting to scrub contaminants from exhaust vents in lieu of carbon or other high cost systems.

Explosion hazards associated with gasoline vapors can be overcome by using intrinsically safe equipment and by ensuring that adequate volumes of air are moved through the system to keep vapor concentrations below the lower explosion limit.

Costs

The major capital costs for soil venting systems are associated with the venting well installation, pump purchase, and the costs associated with air emission control. Venting wells are installed with con-

ventional drilling equipment and materials. Costs for a vent well (20 ft) constructed of 2-in diameter slotted Schedule 40 PVC would be expected to be in the range of $40 per linear foot (lf) installed, and attendant piping would cost approximately $3 to $5/lf. Vacuum pump sizing would be based upon the area and volume of soil to be vented. Vacuum pumps capable of moving 40 to 60 ft^3/min at 1 $\frac{1}{2}$ in. H_2O, similar to that used by Roy F. Weston (1985) in their studies, range in price from $500 to $2,000, and those capable of moving 1,000 standard ft^3/min at 25 in. Hg vacuum, such as that used by Crow et al. (1985), cost approximately $4,000. Operating costs vary depending on utility costs and time of operation. Payne et al. (1986) reported that soil venting was effective in the cleanup of soil contaminated with PERC, and that it was more cost-effective than excavation and removal if soil volumes exceeded 500 yd^3. Anastos et al. (1986) estimated that full-scale remediation of the TCE-contaminated site using soil venting techniques would range in cost from $15 to $20/yd^3 exclusive of air emission treatment costs.

Soil Washing/Extraction

Soil washing is any technique that removes gasoline constituents from the soil matrix by actively leaching the contaminants from the soil into a leaching medium. The extracted constituents can then be removed from the washing fluid by conventional treatment methods. Soil washing is accomplished either in situ as a water flushing system, as shown in Figure 12, or processed through a countercurrent extractor system as shown in Figure 13. Water is the fluid most often used for soil flushing, and it may contain additives such as acids, alkalis, and detergents. However, washing fluids can also consist of pure organic solvents such as methanol, hexane, or triethylamine (TEA).

The slurry of soil and washing fluid can be dewatered by conventional techniques such as sedimentation, filtration, evaporation, dissolved air flotation, or drying beds. The treated soils can then be put back into the original excavation or sent to a sanitary landfill. This technology has been developed extensively in the mining and oil recovery industries to both remove and concentrate gasoline contaminants. The leachate collected from the extraction process can be treated conventionally and recycled in a closed system. Contaminated solvents are separated by physical separation techniques such as distillation, evaporation, or centrifugation.

Treated effluent can be reinjected into the ground; however, this method presumes the need for site controls. Suitable site controls may consist of above- or below-ground barriers.
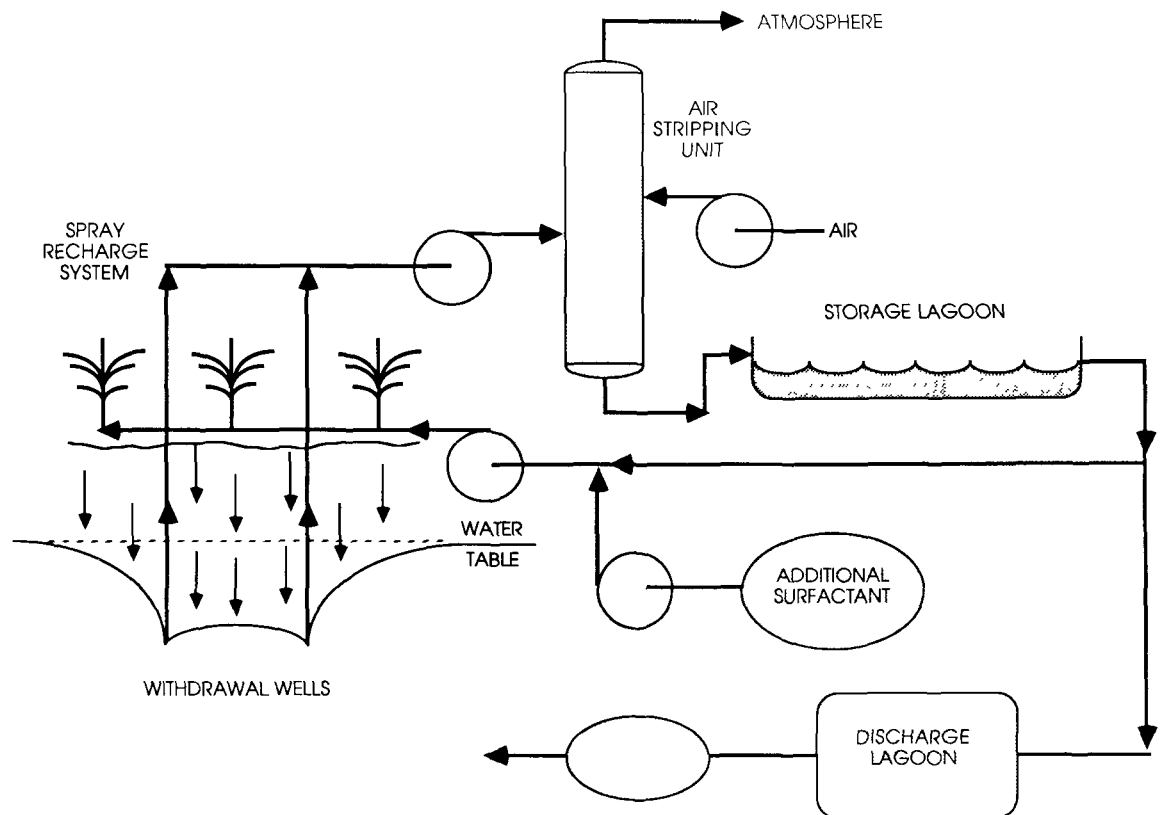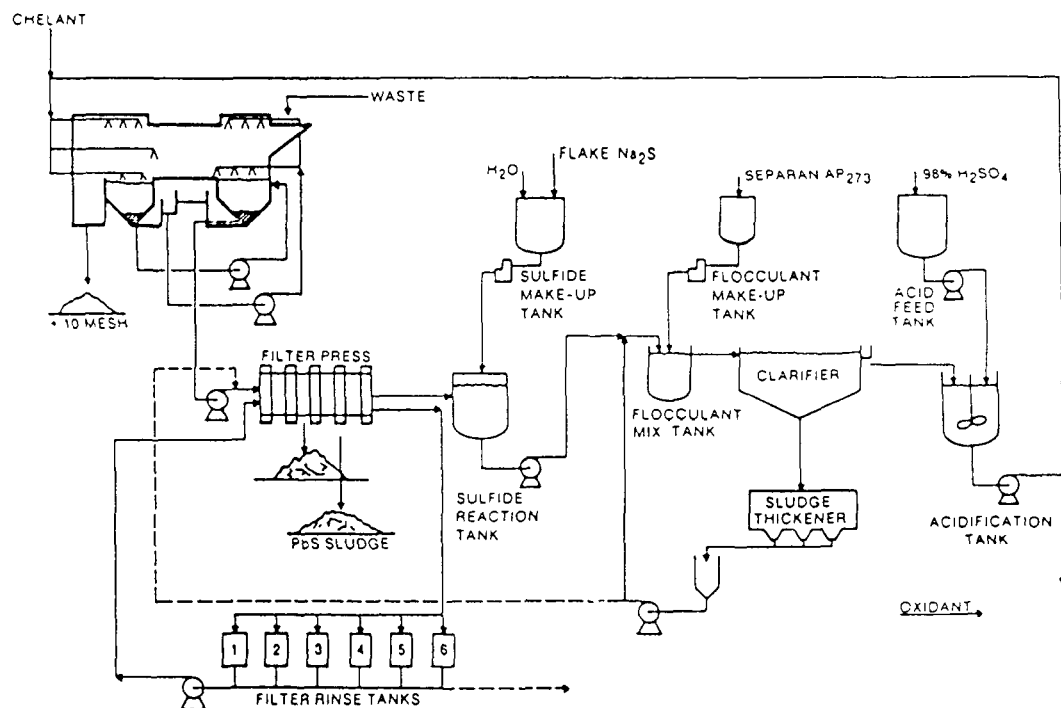
Figure 12. Soil flushing system.

Figure 13. Countercurrent extractor process flow diagram.

Effectiveness

The effectiveness of a soil washing system depends in large part on the residual gasoline capacity of the soil. Creosote-coal tars adhere more tightly to the soil matrix because of their low solubility in groundwater. Diesel, kerosene, and gasoline are not so tightly bound to the soil matrix, and thus the soil washing system is very effective on these constituents.

Richard and Trost (1986) have evaluated the effectiveness of soil washing in several organic contaminated soils. Their system utilizes alkaline agents (such as NaOH and Na_4SiO_4) and biodegradable surfactants to liberate the organic contaminants from the clays and sands. The slurried soil is separated using froth flotation equipment, and the cleaned soils are returned to the site. Test results have shown this soil-washing process will remove up to 99.4 percent toluene, 99.5 percent gasoline, 96.7 percent diesel, 96.1 percent kerosene, 97.4 percent TCE, 99.9 percent tetrachloroethylene, and 99.0 percent creosote-coal tars. However, Richard and Trost caution that the actual percentage of contaminant removal is dependent on the relative amounts of clay and sand, the nature of contaminants, and the concentration and type of reagents.

The Basic Extraction Sludge Treatment (BEST) method developed by Resource Conservation Company (Bellevue, Washington) is a solvent extraction process. The system separates viscous oily wastes into three fractions: clean oil that will be sent to a blending company for use as a fuel; water that can be treated in a biological treatment system; and oil-free, dry solids that can be returned to the site excavation. The key to the process is the use of TEA as the leaching fluid. TEA is completely soluble in water below 66°F but insoluble at higher temperatures. Thus the oils and water from the soils dissolve in the TEA below 66°F. The resulting solids are dewatered conventionally by vacuum filters, filter presses, or centrifuge and then are dried. The solvent-oil-water mix is heated and collected in a decanter where water and TEA separate. Both sludges and soils are currently being treated by this process on a large oil sludge lagoon in Savannah, Georgia.

The process can handle a wide variety of organic wastes and organic-contaminated soils and has resulted in removal rates of up to 99.5 percent of organic constituents such as asphalts, diesel fuels, creosote-coal tars, gasoline, and kerosene.

Limitations

Limitations with the use of soil washing or flushing are associated with soil characteristics that impede the solid-liquid separation after the washing phase.

This may result from a high percentage of silt or clay in the soil material. In situ soil flushing can result in decreased permeability with the use of surfactants or other additives.

Hoag (1985) has found that water used to flush soil residually saturated with petroleum products is not effective in mobilizing the immobile phase, and surfactant treatment may be necessary to remove these materials effectively. Engineering-Science Inc. (1986) in evaluating aquifer restoration techniques found that if the equivalent of 120 years of precipitation was applied to a soil saturated with gasoline, the leachable hydrocarbon fraction decreased from 1,500 ppb to 400 ppb. Gasoline was still detected in the column after flushing with 844 pore volumes. As noted in Table 13, significantly greater volumes of water than air are required to renovate residually contaminated soils.

Whether in situ or excavation systems are utilized, laboratory and pilot testing will be necessary to determine feasibility. Contaminant removal rates may not be adequate to reduce soil contamination below required action levels.

Costs

MTA Remedial Resources, Inc., which has developed a commercial soil washing process, reports processing costs of about $100/ton for both capital amortization and operating costs. This cost does not include excavation or disposal expense. Resource Conservation Co. with its BEST treatment system has estimated a processing cost of about $120 to $150/wet ton. This cost would not include excavation or disposal expense.

Several systems have been employed at hazardous waste sites. A soil washing system that is being tested at Lee's Farm, Wisconsin, has an estimated cost of about $150 to $200/yd^3 excluding development and excavation costs. The major costs are usually associated with the washing fluid treatment system.

Microbial Degradation

Soils harbor a plethora of microorganisms that can degrade hydrocarbons and other environmental contaminants. Soil bacteria, actinomycetes and other microbes, have been shown to acclimate readily to hydrocarbons and to use these compounds in their metabolic processes. Hydrocarbon components acted upon by soil microbial populations under ideal conditions will be converted to microbial biomass and carbon dioxide.

The ability of microbial populations to degrade hydrocarbons has been exploited by the petroleum industry through land farming techniques. In land farming, petroleum refining wastes and by-products

are placed on soils, taking advantage of the ability of indigenous microorganisms to degrade these materials. Whether indigenous or introduced, microbial populations can potentially be used to degrade gasoline-contaminated soil in situ or in a reactor or otherwise modified environment. This section discusses the principles involved in biodegradation and issues relevant to the use of such systems.

The scientific literature is replete with laboratory research reports on the biodegradation of gasoline in soils and aqueous systems. The American Petroleum Institute (API) has compiled much of this information in two publications (Brookman et al., 1985a and 1985b).

Although the laboratory research summarized in these documents provides useful data for developing corrective action strategies, field application data are somewhat more limited.

Effectiveness and Limitations

Bossert and Bartha (1984) report that n-alkanes, n-alkylaromatics and aromatic petroleum components of the C_{10} to C_{22} range are the least toxic and the most readily biodegradable of the petroleum components, whereas those in the C_5 to C_9 range have relatively high solvent type membrane toxicity. Those petroleum components above C_{22} have low toxicity but are not readily degraded because of their physical characteristics. Cycloalkanes and branched alkanes in the C_{10} to C_{22} range are more resistant to biodegradation than aromatics and n-alkanes due to their branched nature.

Gasoline composed principally of alkanes in the C_5 to C_{10} range and cycloalkanes would therefore be expected to be subject to microbial degradation in the soil environment provided conditions were not limiting. According to Brookman et al. (1985b), factors that affect the rate at which degradation will occur include:

• Indigenous soil microbial population

• Hydrocarbon type and concentration

• Soil extraction, expressed as pH

• Nutrient availability

• Temperature

• Moisture content

• Oxygen content

These factors are discussed in the following subsections.

Indigenous Soil Microbial Population

Soil microbes capable of degrading petroleum products include Pseudomonas, Flavobacterium, Achromobacter, Arthrobacter, Micrococcus and

Acinetobacter, among others. In fact, more than 200 soil microbial species have been identified which can assimilate hydrocarbon substrates (Savage et al., 1985). Although numerous methods are available to enumerate the microbial population in soil, it is questionable if such determinations are of value in implementing corrective actions. Total microbial counts of fertile soils range from 10^7 to 10^9 per gram of dry soil, and hydrocarbon degraders counts range from 10^5 to 10^6 per gram in soils with no history of pollution (Bossert and Bartha, 1984). Soils which have been exposed to petroleum have counts on the order of 10^6 to 10^8 per gram. Indigenous soil microbial populations would therefore be expected to respond to releases of gasoline provided that environmental conditions support growth.

Microbial populations can also be augmented by the introduction of acclimated microbes. Acclimated microorganisms are receiving increased attention for use in degrading hydrocarbons in soils. Acclimated microorganisms are developed through genetic manipulation or enrichment culturing techniques. Some firms that sell microbial cultures or systems that use indigenous organisms or enrichment processes to degrade environmental contaminants are:

PolyBac Corporation
Allentown, Pennsylvania

Groundwater Decontamination Systems, Inc.
Paramus, New Jersey

Solmar Corporation
Orange, California

Although Wilson et al. (1986) acknowledge that acclimated microorganisms have been used successfully to degrade hydrocarbons in soils, they identify the following obstacles to aquifer restoration:

• Acclimated microbes must be able to survive in the environment and compete successfully with indigenous microbes for nutrients.

• Acclimated microbes must be able to move from point of injection to location of contaminant.

• Acclimated microbes must retain selectivity for degrading compounds for which they were initially adapted.

These same obstacles to restoration would be expected in soils to some extent. However, should the soil be amenable to mechanical mixing, some of these limitations could be overcome.

Hydrocarbon Type and Concentration

Although indigenous soil microbes and introduced microorganisms can theoretically degrade gasoline

in soil, the concentration of the products in the soil may limit the rate of degradation. Alexander (1985) has reported that microbes may not assimilate carbon from chemicals in trace amounts in natural environments. Co-metabolism, the process by which a microbe oxidizes a substance without being able to use the energy derived from the oxidation to support its growth, may be the primary mode of degradation of hydrocarbons at parts-per-billion levels (1 ppb = 1 μg/L).

White et al. (1985) used soil samples obtained from gasoline spill sites in Virginia, Pennsylvania and New York to demonstrate reduction of methanol from 105 mg/L to 0 mg/L in 30 days and of TBA, a gasoline additive, from 115 mg/L to 0 mg/L in 55 days.

Bossert and Bartha (1984) report that when petroleum is added to soils at rates of 0.5 to 10 percent by weight, rates of degradation are limited in the first 30 to 90 days by factors other than substrate availability, whereas at later stages of degradation at extremely low petroleum addition rates, substrate availability limits the rate of degradation.

Overash and Pal (1979) indicate that a soil's capacity to assimilate oil in land treatment systems ranged from 0.2 to 0.4 percent per month by weight.

Soil Reaction

Soil reaction, expressed as pH, can influence the rate at which gasoline is degraded by microorganisms. Optimal oil sludge degradation has been demonstrated to occur between pH 7.5 and 7.8 (Atlas, 1981). Under acidic soil conditions, fungi will be more prevalent than bacteria. Although fungi can degrade petroleum products, the rate of degradation will be less than that attained by a mixed fungi-bacterial community such as would occur in neutral to slightly alkaline soils (Bossert and Bartha, 1984).

Nutrient Availability

The availability of the soil micronutrients nitrogen and phosphorus are often cited as being rate-limiting to hydrocarbon degradation. The availability of macronutrients present in soil to microbes is optimum at near neutral pH values, although in some soils the nutrient status may be low. The optimal quantity of nitrogen and phosphorus required for microbial degradation is related to the organic carbon content of the soil-waste mixture. According to Bartha and Bossert (1981) the optimum organic carbon/nitrogen/phosphorus ratio for oil sludge degradation is 60/1/0.075.

Temperature

The majority of microorganisms responsible for degradation of petroleum hydrocarbons are mesophiles (30°C) and thermophiles (40°C), although degradation by psycrophiles (4°C) has been reported (Bossert and Bartha, 1984). Reportedly, optimum temperatures for microbial degradation are above 20°C (Atlas, 1981), although significant increases in degradation rates above 40°C have not been widely reported. Soil temperatures in the continental United States during all but winter months in northern latitudes, therefore, should not limit microbial degradation.

Moisture Content

Microbes require water to carry out metabolic processes. The amount of water a soil contains varies with time in response to precipitation, drainage, and evapotranspiration. The quantity of moisture retained by soil after free drainage is termed field capacity, whereas the total amount of water a soil can hold at saturation is termed moisture-holding capacity. Optimal microbial activity occurs between 50 and 80 percent water-holding capacity, and at 10 percent or less, metabolic activity becomes marginal (Bossert and Bartha, 1984).

Oxygen Content

Lack of oxygen is normally the rate limiting factor for aerobic hydrocarbon degradation in most soil situations (Nyer, 1987). Product leakage into soils may effectively fill pore spaces with liquid and gaseous components, thus excluding oxygen. A high water table or wet soil conditions can further exacerbate the oxygen supply.

As soils become saturated, anoxic conditions result and anaerobic microbial activities predominate. Although some studies indicate that anaerobic degradation of petroleum products does occur, the rate at which these reactions occur is significantly less than that encountered under aerobic conditions. Therefore microbial degradation of gasoline under negative redox potentials would not be expected to be significant. The redox potential is an electric potential established by the ratio of oxidized materials to reduced materials in a soil system. Aerobic environments are generally characterized by redox potentials in the positive range, whereas anaerobic environments are characterized by negative values.

Lack of oxygen in aquifer systems has been reported as a major limiting factor for in situ aquifer microbial degradation of petroleum products. Wilson et al. (1986) note that microorganisms in a well-oxygenated groundwater containing 4 mg/L of oxygen can degrade only 2 mg/L of benzene and that the solubility of benzene in water (1,780 mg/L) is much greater than its capacity for degradation.

Yaniga and Smith (1985) reportedly used mechanical systems to add air to the aquifer but were able

only to induce 10 ppm of oxygen (roughly the saturation concentration of oxygen in water at 20°C) into the groundwater. To overcome the limited efficiency of the system due to insufficient oxygen, injection of hydrogen peroxide to the groundwater was investigated. Hydrogen peroxide injected at concentrations of 100 ppm stimulated microbial degradation. According to Raymond (1987), hydrogen peroxide can increase dissolved oxygen in groundwater to between 250 and 400 ppm. Liquid oxygen may also be injected and can result in dissolved oxygen concentrations of about 40 ppm.

Chan and Ford (1986) reported on the use of in situ soil techniques and a bioreactor to degrade No. 2 fuel oil that had leaked from storage tanks. The field application of these techniques convinced them that the bioreactor was at least four times more efficient than in situ methods due to higher oxygen content (9 mg/L vs 2.5 mg/L in the water).

Borden and Bedient (1986) developed theoretical equations for simulating the simultaneous growth, decay, and transport of microorganisms as well as transport and removal of hydrocarbons and oxygen in aquifer systems. Based on their studies, they concluded:

• A zone of reduced hydrocarbon and oxygen concentration will develop between the oxygenated formation water and the plume in which microbial degradation rates are reduced.

• A large microbial population will develop in the region contiguous to the hydrocarbon source in

which an instantaneous reaction of hydrocarbons and oxygen takes place.

• Adsorption to the aquifer material may significantly enhance the biodegradation of hydrocarbon spills.

• Exchange of oxygen and hydrocarbon vertically with the unsaturated zone may significantly enhance the rate of biodegradation.

This study and the accompanying study on field application of the model (Borden et al., 1986) point out the importance of oxygen exchange to microbial degradation in aquifer materials. In soil materials above the water table, the rate of oxygen exchange will be greater than that associated with aquifer materials. The rate at which oxygen can be brought into contact with the microbial population and gasoline-contaminated soils will be related to the depth of contamination, the texture of the soil, and its water and gasoline content. Table 13 provides a comparison of the amounts of air or water required to be exchanged with soil materials in order to renovate residually saturated soils (Wilson and Ward, 1986). These values were developed based upon the assumption that the oxygen content of air was 200 mg/L and that of water was 10 mg/L and that the hydrocarbons were completely metabolized to carbon dioxide. Wilson and Ward caution that actual values at specific sites would vary from these typical estimates. Nonetheless, this information further points out the significance of oxygen in the degradation of hydrocarbons.

Table 13
Estimated Volumes to Renovate Hydrocarbon Residually Saturated Soils

Texture	Proportion Occupied by			Pore/Volumes	
	Hydrocarbons[1]	Air[1]	Water[2]	Air	Water
Stone to coarse gravel	0.005	0.4	0.4	250	5000
Gravel to coarse sand	0.008	0.3	0.4	530	8000
Coarse to medium sand	0.015	0.2	0.4	1500	15000
Medium to fine sand	0.025	0.2	0.4	2500	25000
Fine sand to silt	0.040	0.2	0.5	4000	32000

Source: Wilson and Ward, 1986.
[1]Drained
[2]Saturated

50

Costs

Costs for microbial degradation of gasoline-contaminated soil are not widely reported because these techniques are most often applied to remediate groundwater systems or recirculation systems. FMC provided cost estimates ranging from $400,000 to $600,000 to clean up a hypothetical spill of 10,000 gal of jet fuel in a fine gravel formation using their hydrogen peroxide enhanced microbial degradation system. (FMC's Groundwater Remediation Operations have recently been acquired by International Technology.) Olsen et al. (1986), however, report that bioreclamation costs are in the range of $50 to $100/ton ($66 to $123/yd^3).

Summary

Soils saturated with gasoline will drain under the forces of gravity until they reach a point called residual saturation. At that point the gasoline retained in a soil normally does not migrate to groundwater supplies as free product. However, infiltrating rainfall or fluctuating water tables can flush gasoline from the soil matrix or transport components in a dissolved phase. Gasoline present in unsaturated soils, however, may migrate to groundwater supplies and pose health risks, or it may migrate as vapors to enclosed structures and pose explosion hazards. Thus corrective actions that effectively mitigate these risks need to be considered under corrective action programs for leaking USTs.

The corrective actions that are potentially applicable to soils contaminated with gasoline include excavation and disposal, enhanced volatilization, incineration, venting, flushing (washing), and biodegradation. In certain instances, other corrective actions such as in situ stabilization may also be appropriate. However, because of the relatively high volatility of gasoline and the ability of microbes to degrade its components, corrective actions which render the contaminated materials less hazardous should be favored. Table 14 summarizes the major issues associated with the corrective actions for gasoline-contaminated soils.

Excavation and disposal is probably the most widely used corrective action to recover and treat contaminated soil at UST sites at the present time. Various contractors contacted indicated that soils were typically disposed at landfills with reported tipping fees in some cases as low as $12/yd^3. Excavation and disposal costs may approach $200 to $300/yd^3, however. Therefore, this alternative is cost inefficient for all but small quantities of soil. In situ venting is more cost-effective for treating soil contaminated with volatiles when volumes exceed

500 yd^3. Increasing costs and disposal restrictions will make this alternative less attractive in the future.

States exercise varying degrees of control of the disposal of gasoline-contaminated soils. This situation leads to the export of soil from states with more stringent controls to those that are less restrictive. Uniform guidelines for disposing contaminated soils would minimize these types of practices and thus serve to minimize risks associated with transport over long distances.

Disposing contaminated soils in batch asphalt plants is a practice that is not reported in the literature but apparently is another widespread method of disposal. A number of contractors reported that asphalt plants accepted gasoline-contaminated soils and, in certain states, at fees of about $55/yd^3. In other states with more stringent regulations, asphalt plants will not accept gasoline-contaminated soils because they would then be classified as hazardous waste treatment facilities and subject to all pertinent regulations.

One asphalt plant reported that tests required before the soil was accepted included EP toxicity, flash point, and priority pollutant analyses. Those materials considered toxic or which contained chlorinated solvents were not accepted.

Excavation and disposal may be an appropriate corrective action when undertaken simultaneously with removal of leaking USTs. However, because this action results in significant disturbance of surface and subsurface infrastructure, it may not be applicable in certain settings. Disposal of the contaminated soils also carries with it potential liabilities attendant to its ultimate disposition. Treatment technologies which provide for destruction or detoxification of the soil materials such as enhanced volatilization, incineration, or biodegradation would therefore be favored means of disposal provided they are cost-effective.

Enhanced volatilization can be accomplished by simply turning the contaminated soils and thereby increasing exposure of the gasoline to the atmosphere; or by using mechanical systems with a heat source to drive the volatile compounds from the soil. The latter technique is referred to as low temperature thermal stripping and has the greatest flexibility and control in system operation. In this system, gases volatilized from the soil can be captured and destroyed rather than discharged to the atmosphere as would occur with a rototilling operation. The low temperature thermal stripping system is capable of removing 99.99 percent of volatile organic compounds including BTX. Cost estimates for processing soil using low temperature for this

Table 14
Soil Correction Action Summary Evaluation

Method	Typical Cost ($/cubic yd)	Effectiveness	Limitations	Applicability and Relative Use at UST Sites	Non-UST Sites Presently Using Method
Excavation and disposal	$50-300	Reduction in mobility. Reduction in volume. 100% removal of contaminants in soil excavated.	Brings contaminant to surface, thereby possibly increasing exposure. Not efficient if large quantities are to be removed. Significant amounts of surface area disturbed relative to depth excavated. Difficult to undertake in heavily urbanized areas near buildings, utilities. Requires suitable means of disposal.	High Widely used	At least 14 sites
Enhanced volatilization	$250	Reduction in toxicity. 99.99% removal of VOC's. Most effective if 15,000 to 80,000 tons of soil require treatment.	Requires vapor phase treatment and dust control.	Medium Limited use	Mckin, ME Metaltee Aerosystems, NJ Caldwell Trucking, NJ Triangle Chem, TX Hollingsworth Solderless, FL
Incineration	$600 +	Reduction in volume. Reduction in mobility. Total destruction of all contaminants.	Permitting requirements can be significant. Brings contaminants to surface thereby possibly increasing exposure. Typically the most expensive soil treatment technology. Appropriate usually when toxics other than just volatiles are present.	Low Limited use	At least 28 sites
Active venting	$15-20	Reduction in mobility. 99.99% removal of VOC's.	Effectiveness depends on soil characteristics. May require vapor phase treatment of emissions. Care must be taken to avoid explosions.	High Some cases	Tyson's Dump, PA Verna Well Field, MI Ponder's Corner's, WA
Passive venting	$10-15	Reduction of mobility.	May require vapor phase treatment. Not as effective as active venting.	High Some cases	At least 5 sites
Soil washing	$150-200	Reduction of mobility. 99.99% removal of contaminants. Accelerated removal of contaminants.	Requires separation techniques such as distillation, evaporation, centrifugation. Less effective for textured soils.	Low Limited use	Leeds, AL Goose Farm, NJ Lee's Farm, WI Bog Creek Farm, NJ Western Processing, WA Volk Air Field, WI
Microbial degradation	$60-125	Reduction in toxicity. Variable effectiveness.	Biologic systems subject to upset.	High Some use	At least 7 sites.

52

system range from $245 to $320/yd³ including air emissions control.

Incineration techniques can provide destruction removal efficiencies (DRE) in excess of 99.99 percent; however, the added costs associated with incineration and the permitting process which may be attendant to the use of mobile units would suggest that this type of corrective action is not appropriate unless the soil is also contaminated by constituents that render it toxic or otherwise untreatable. Incineration costs range from $200 to $640/yd³ exclusive of costs of transportation and final ash disposal.

Soil venting systems have demonstrated 99 percent effectiveness in certain applications. These techniques are relatively easy to implement and cause minimal disturbance to structures or pavement. Soil venting is also easily incorporated into systems for cleanup of contaminated aquifers. There is much uncertainty regarding the overall effectiveness of soil venting systems, however, because the technology has not been widely applied. Unit costs for soil venting have been reported to be as low as $15 to $20/yd³ of soil treated exclusive of air emission control costs.

Soil flushing (washing) systems may provide for effective removal of contaminants in certain hydrogeologic settings at competitive rates. However, because this operation further disperses contaminants, its usefulness should be carefully evaluated in light of the potential for exacerbating the problem. Costs for soil washing range from $150 to $200/yd³ exclusive of excavation costs.

Biodegradation of gasoline by indigenous or introduced soil microorganisms is effective in unsaturated soils provided environmental conditions can sustain microbial metabolism. Lack of oxygen may be the factor that most limits degradation in subsurface soils. Costs for microbial degradation of petroleum products in soil range from $66 to $123/yd³ making this one of the least costly of the corrective actions evaluated. However, because in situ degradation techniques are akin to "black boxes," they require extensive monitoring networks to demonstrate effectiveness. The biological systems associated with these techniques must be carefully nurtured to ensure optimal performance.

Although a number of soil treatment techniques are available for removing gasoline from soil, only a few have been applied in the field. This is largely because of uncertainties regarding the effectiveness of soil treatment technologies like venting and biodegradation. Unlike groundwater treatment technologies, where the science is well understood and the principal design parameters are well known, soil treatment techniques are considered

"black boxes." Other soil treatment technologies such as incineration and soil washing are expected to have only limited applicability to cleanup of leaking USTs, either because they are prohibitively costly or because they create other undesirable environmental problems.

Even though excavation and landfilling are the most widely used corrective action for soils, this approach may not be the best solution for soil cleanup. Because of time delays at local landfills, excavators have had to store large piles of contaminated dirt, and it is not known to what extent vapors emanating from these dirt piles present a health hazard. This concern exists for any corrective action that necessitates bringing contaminated soil to the ground surface.

Although the two technologies have not been fully developed, it appears that a combination of soil venting and microbial degradation may provide the most efficient corrective action because they limit the public's exposure to the contaminated substances. Further research is needed, however, to confirm the effectiveness of these two techniques.

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Section 5
Removing Gasoline Dissolved in Groundwater

For removal of gasoline constituents dissolved in groundwater several methods are available: air stripping, activated carbon adsorption, biorestoration, resin adsorption, reverse osmosis, ozonation, oxidation with hydrogen peroxide, ultraviolet irradiation, and land treatment. Under the right circumstances any of these methods can remove, destroy, or detoxify all or some of the gasoline contaminants. Air stripping and activated carbon adsorption are the most cost-effective and widely applied in practice, however, and have been used in over 95 percent of groundwater cleanups. Together air stripping and activated carbon adsorption are applicable to most cases where gasoline has contaminated local groundwater. They offer the best combination of effectiveness in removing contaminants to low levels over a wide range of situations, as well as being fairly cost-effective.

Biorestoration is a technology that has only recently begun to receive attention. Its potential, although promising, has yet to be proven as a viable, widespread method for controlling groundwater contaminants because of an inability to predict and model the timing, kinetics, or reduction that is due to biorestoration. The other methods mentioned may be effective in certain situations but are expected to be used rarely at leaking UST sites because of their limitations and/or their high cost.

The following subsections address air stripping, carbon adsorption, and biorestoration in terms of their operation, removal efficiencies, cost-effectiveness, and limitations.

Air Stripping

Background

Air stripping is a proven, effective means to remove volatile organic compounds (VOCs) from groundwater. It works by providing contact between air and water to allow the volatile substances to diffuse from the liquid to the gaseous phase. In many cases it is the most cost-effective option for gasoline-contaminated groundwater. It has been used at many sites, either alone or with other methods (usually activated carbon); and with effectiveness. There are several methods of air stripping, including diffused aeration, tray aerators, spray basins, and packed towers.

Diffused Aeration

In a diffused aeration system, air (usually compressed air) is injected into the water through a diffuser or sparging device that produces fine bubbles. Mass transfer occurs across the air-water interface of the bubbles until they leave the water or become saturated with contaminant. This type of aeration is usually conducted in a contact chamber, although it can take place in holding ponds. A schematic diagram of a diffused aerator appears in Figure 14.
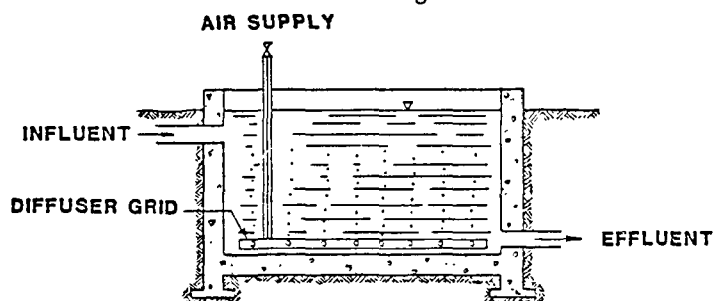

Figure 14. Schematic of a typical diffused aerator.

Mass transfer rates can be improved by producing smaller bubbles, increasing the air-water ratio, improving basin geometry, or using a turbine to increase turbulence. Increasing the depth of the tank will also improve the mass transfer rate if the bubbles do not reach saturation before exiting to the atmosphere (Kavanaugh and Trussell, 1981).

In practice, diffused aerators have removal efficiencies in the range of 70 to 90 percent for organics such as trichloroethylene, carbon tetrachloride, tetrachloroethylene, and vinyl chloride (Kavanaugh and Trussell, 1981; Dyksen et al., 1985). In some cases this may be an acceptable level of treatment; where higher removal rates are required, though, diffused aerators are not practical.

Tray Aeration

Tray aeration is a simple, low maintenance method of aeration that does not use forced air. Water is allowed to cascade through several layers of slat trays to increase the surface area available to the atmosphere (Figure 15). Full-scale tray aerators used for the removal of trichloroethylene, tetrachloroethylene, trans-1,2-dichloroethylene, 1,2-dichloroethane, and other chemicals have shown removal efficiencies of 10 to 90 percent; usual values are between 40 and 60 percent (Hess et al., 1983). In certain situations, tray aeration could be a cost-effective method of reducing somewhat the VOC concentrations (for example, prior to activated carbon treatment). Like diffused aeration, this method cannot be used where low effluent concentrations are required; it has not been widely applied at leaking UST sites.
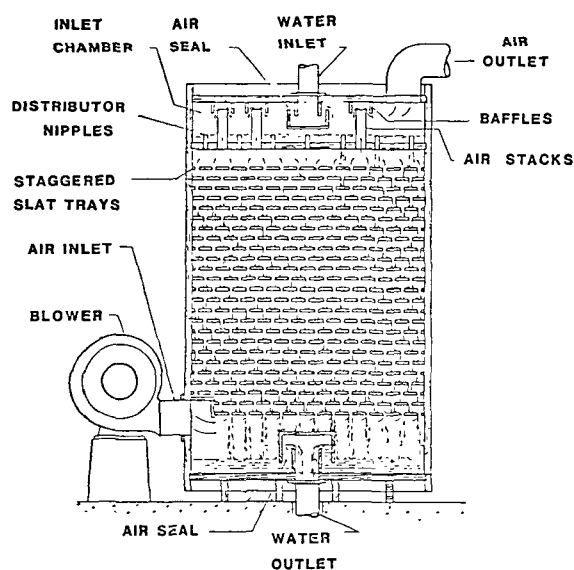

Figure 15. Schematic diagram of redwood slatted tray aerator.

Spray Aeration

Spray aeration involves setting up a grid network of piping and nozzles over a pond or basin. Contaminated water is simply sprayed through the nozzles and into the air to form droplets. Mass transfer of the contaminant takes place across the air-water surface of the droplets. Mass transfer efficiency can be increased by passing the water through the nozzles multiple times; removal of 1,1,1-trichloroethane is reported to have increased from 40 percent to 85 percent by passing water through nozzles two-and-a-half times (Hess et al., 1983). Spray aeration has also been used as a means of aquifer recharge; water treated by granulated activated carbon (GAC) and air stripping was sprayed over an 8-acre area to recharge the aquifer being cleaned (McIntyre et al., 1986).

Spray aeration could result in higher removal of VOCs, as well as an increased rate of aquifer restoration due to the recharge. Two disadvantages of spray aeration are, however, the large land area necessary for the spray pond and the formation of large amounts of mist that could be carried into nearby residential areas. Also, the possibility of ice formation (both of the mist and on the nozzles) would lower the usefulness of this technique in colder climates.

Packed Towers

The packed tower method involves passing water down through a column of packing material while pumping air countercurrently up through the packing (Figure 16). The packing material breaks the water into small droplets, causing a large surface area across which mass transfer can take place. This high air-water ratio and the large void volume can result in very high removal efficiencies, greater than those attainable by any other aeration technique.

These countercurrent packed towers are the most common of the air stripping methods; in fact, the term "air stripping" often refers to packed tower aeration. The towers are very effective in removing VOCs; reported removal efficiencies can reach as high as 100 percent (i.e., to not-detectable levels), but are typically in the range of 90 to 99 percent for the compounds normally found at gasoline-contaminated sites. Packed towers are also the most cost-effective of the air stripping methods for most situations. For these reasons, this section of the manual focuses on countercurrent packed towers.

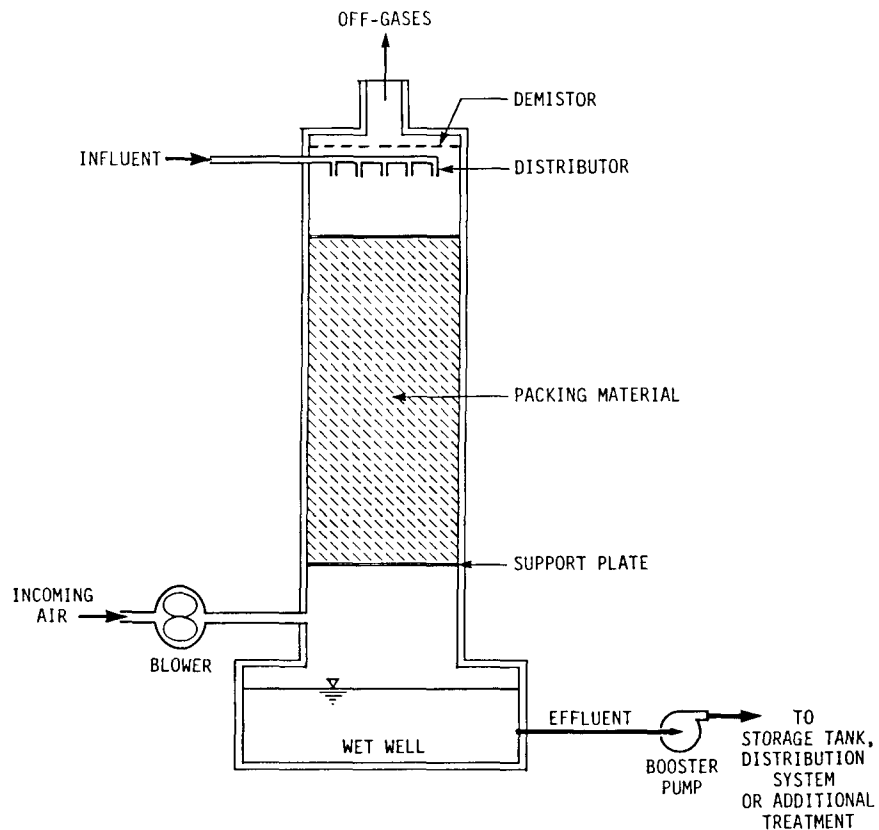Figure 17 shows graphically the VOC removal ranges for feasible aeration alternatives.

Figure 16. Schematic diagram of packed tower aerator.
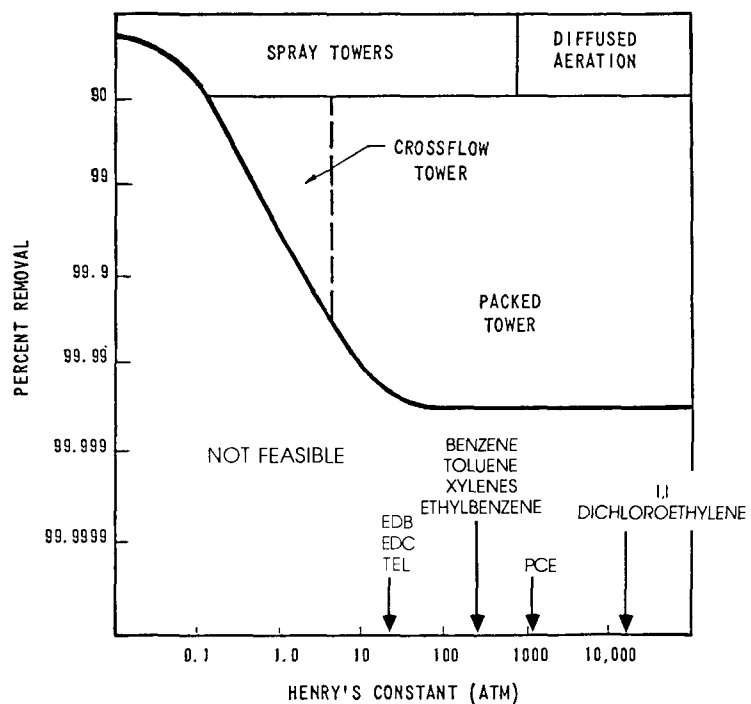

Figure 17. Ranges for feasible aeration alternatives for the removal of volatile compounds.

Theory of Air Stripping

The basic principles of air stripping are straightforward (Treybal, 1980). The kinetic theory of gases holds that molecules of dissolved gases can pass freely between the gaseous and liquid phases. At equilibrium, the same number of molecules move in both directions through a unit of area in a unit of time. The departure from equilibrium provides the driving force for the mass transfer. The rate of mass transfer is proportional to the difference between the liquid-phase concentration of a contaminant in the influent (the operating concentration) and that substance's equilibrium liquid-phase concentration. The equilibrium concentration of a contaminant depends on its Henry's law constant. Henry's law describes the relative tendency for a substance to separate between the liquid and gaseous phases at equilibrium. Thus, Henry's constant can be thought of as a partitioning coefficient. As will be discussed later, the magnitude of Henry's constant is integral to the feasibility of air stripping for a particular compound. Henry's law can be expressed mathematically as:

$$p_a = HX_a \qquad (1)$$

where

p_a = Partial vapor pressure of contaminant a (atm)

H = Henry's law constant (atm)

X_a = Mole fraction of contaminant a in water (mole/mole)

The phenomenon of air stripping can best be described as "controlled disequilibrium." Introducing fresh, contaminant-free air into the system results in a net mass transfer from the liquid phase to the gaseous phase. By continually replenishing the air with contaminant-free air, the contaminants are eventually reduced to very low levels.

Design Parameters

The design of an air stripping tower can also be described mathematically; the equations are well-developed in the literature (Treybal, 1980; Kavanaugh and Trussell, 1981; Hand et al., 1986). The equations are derived by setting up a mass balance in the air stripper (Figure 18). Four basic assumptions are incorporated in these equations. First, that the influent air is free of VOCs. Second, that plug flow conditions (i.e., where there is no differential flow) hold for the air and water flow. The use of an inlet water distribution system (weir tray or nozzles) helps to preserve this condition. Third, that the changes that occur in the liquid and air vol-
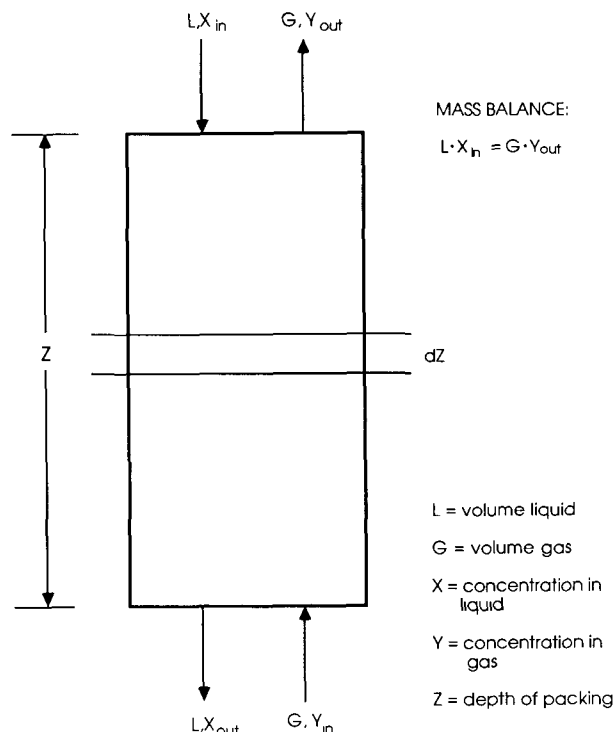

Figure 18. Differential element for an air stripping tower.

umes during mass transfer are negligible. Fourth, that Henry's law holds true for these conditions.

To solve for the master design equation, two variables first need to be determined: the flow rate to be treated and the percent removal desired. The flow rate depends on many factors, such as the extent of the contamination, the rate at which the contaminant plume is migrating, the future use of the water, and the physical characteristics of the aquifer (its permeability or transmissivity). The desired removal efficiency is strongly dependent on the future use of the water as well as the immediate health threat posed by the contamination.

The remaining design parameters can be determined once the flow rate and desired removal efficiency are known. When designing a tower for a specific removal efficiency, a number of parameters (e.g., size and type of packing, height and/or diameter of the column, water temperature, air-water ratio, gas pressure drop) can be adjusted to achieve similar results. Some of these, such as air-water ratio and tower height, are inversely related. The objective of the design of an air stripping tower is to maximize the rate of contaminant removal from the water at the lowest reasonable cost. This is usually done by iterating various parameters to find the best combination.
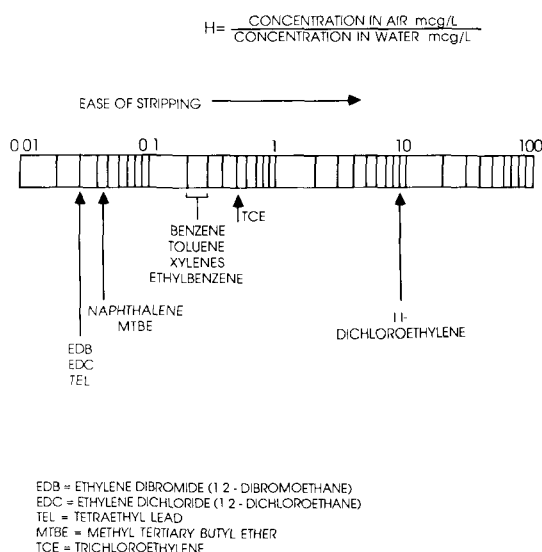
The required design parameters are Henry's constant (which is both contaminant- and temperature-dependent), the mass transfer coefficient (which is
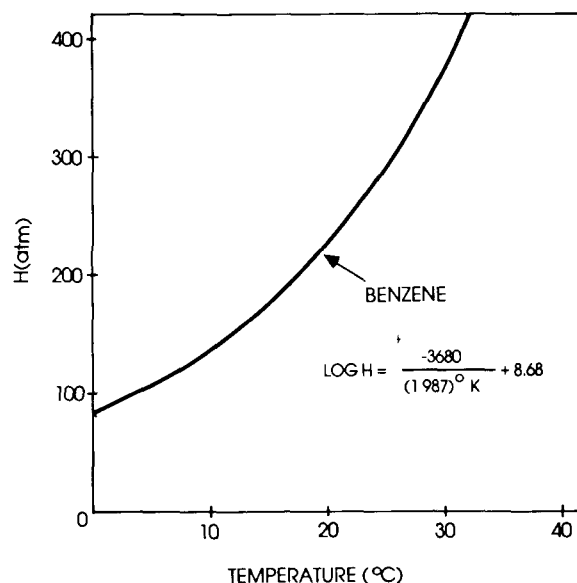
dependent primarily on the packing material), and the stripping factor and the air pressure drop (both of which are selected to minimize total cost while satisfying the removal efficiency goals).

Henry's Law Constant

Theoretical Henry's constants are available in the literature for most compounds of interest (ICF, 1985; Perry and Chilton, 1973). Figure 19 shows some Henry's constants, including several gasoline constituents as well as trichloroethylene (TCE) and 1,1-dichloroethylene. These values are computed from data on a compound's gram-molecular weight, water solubility data, temperature, and the equilibrium vapor pressure of pure liquid. The concern has been expressed that Henry's constants derived from these values may not extrapolate correctly to field design work. The low-solute concentration typical of groundwater, the temperature dependence of Henry's constant, and the fact that the inside of an air stripper does not represent true equilibrium are all reasons given to cast doubt on laboratory data. Recent work by Munz and Roberts (1987) has shown that solute concentrations do not affect Henry's constant, however, at least to concentrations as low as 0.001 molar. Temperature was again shown to have a major effect on Henry's constant and thus on stripper performance (Figure 20). Munz and Roberts state that each rise of 10°C in temperature corresponds to an increase in the Henry's constant by a factor of 1.6. Thus, temperature is very important when designing a stripping tower.

$$H = \frac{\text{CONCENTRATION IN AIR mcg/L}}{\text{CONCENTRATION IN WATER mcg/L}}$$

EASE OF STRIPPING ────────▶

EDB = ETHYLENE DIBROMIDE (1 2 - DIBROMOETHANE)
EDC = ETHYLENE DICHLORIDE (1 2 - DICHLOROETHANE)
TEL = TETRAETHYL LEAD
MTBE = METHYL TERTIARY BUTYL ETHER
TCE = TRICHLOROETHYLENE

Figure 19. A comparison of stripping rates for TCE and gasoline compounds.

Figure 20. Temperature dependence of Henry's law constant.

Henry's law constants are typically expressed as either "dimensionless" or in atmospheres. Dimensionless units are valid only for systems that operate at standard pressure because the actual units are:

(atmospheres of pressure) $\dfrac{\text{cubic meters of water}}{\text{cubic meters of contaminant}}$

Typical ranges of "dimensionless" Henry's constants for gasoline components are 0.02 to 0.30 (see Figure 19).

The more common unit, atmospheres, is expressed by:

(atmospheres of pressure) $\dfrac{\text{moles of water}}{\text{moles of contaminant}}$

Typical values for gasoline components (expressed in atmospheres) range from 20 to 500 (Figure 17). It is very important when designing air strippers to use correct units for Henry's constants.

Mass Transfer Coefficient

The rate of mass transfer per unit time per unit volume is first-order, proportional to the difference between the liquid-phase concentration of the contaminant in the influent and the equilibrium concentration:

$$J_A = -K_l a(C_i{}^* - C_i) \qquad (2)$$

where

J_A = the rate of mass transfer of contaminant A $(kg/hr/m^3)$

$K_l a$ = the mass transfer coefficient (K_l) and the specific interfacial surface area (a) $(K_l a$ is also known as the proportionality constant.)

C_i^* = equilibrium liquid-phase concentration (kg/m^3)

C_i = operating liquid-phase concentration (kg/m^3)

The proportionality constant, $K_l a$, is composed of the overall liquid mass transfer coefficient and the specific interfacial area. The mass transfer coefficient, K_l, represents the rate at which the system moves towards equilibrium. The specific interfacial area, a, is a measure of the available total surface area of water that is exposed to the air. This value is dependent on the packing material. The best packing material will optimize the surface area per volume (m^2/m^3).

K_l is a function of the geometry and physical characteristics of the system, the compound being stripped, and the temperature and flow rate of the liquid.

To describe the kinetics of air stripping, the two-phase resistance model of mass transfer is generally used (Perry and Chilton, 1973). This model incorporates the resistance to mass transfer in both the liquid and gas phases. K_l is related to these by:

$$\frac{1}{K_1} = \frac{1}{k_1} + \frac{C_o}{k_g H} \tag{3}$$

where

K_l = overall liquid mass transfer coefficient

k_l = liquid-phase diffusional resistance

k_g = gas-phase diffusional resistance

C_o = molar density of water (55.6 kmole/m^3)

H = Henry's constant (atm)

When a compound has a large Henry's constant (above 50 atm), the term including k_g is negligible. In this case, $K_l \sim k_l$. In these applications, it is valid to assume that the liquid-phase resistance dominates.

Values for $K_l a$ are sometimes supplied by manufacturers or may be found in the literature. However, because of the importance of this parameter in packed tower design, it is recommended that $K_l a$ values be determined from pilot studies.

In the absence of field data, there are two general methods by which these values can be determined. The first is the Sherwood-Hollaway empirical correlation:

$$\frac{K_1 a}{D_w} = x \left[\frac{L'}{u_1} \right]^{1-n} \left[\frac{u_1}{p_1 D_w} \right]^{0.5} \tag{4}$$

where

D_w = molecular diffusion coefficient in water (ft^2/hr)

x, n = empirical constants

L' = liquid mass flux rate $(lb/ft^2/hr)$

u_l = viscosity of water

p_l = density of water

$K_l a$ = units of sec^{-1}

A second, more common method is the Onda equations (Onda et al., 1968). These equations estimate the wetted surface area of the packing material and the liquid-phase and gas-phase mass transfer coefficients. These values are then used to obtain $K_l a$:

$$k_1 = 0.0051 \left(\frac{u_1 g}{p_1} \right)^{\frac{1}{3}} \left(\frac{L}{a_w u_1} \right)^{\frac{2}{3}} \left(\frac{u_1}{p_1 D_w} \right)^{-0.5} \left(a_t d_s \right)^{0.4} \tag{5}$$

$$\frac{a_w}{a_t} = 1 - \exp\left(-1.45 \left[\frac{T_c}{T_w} \right]^{0.75} \left[N_{Re} \right]^{0.1} \left[N_{Fr} \right]^{-0.05} \left[N_{We} \right]^{0.2} \right) \tag{6}$$

$$k_g = 5.23 \left(a_t D_a \right) \left(\frac{G}{a_t u_G} \right)^{0.7} \left(\frac{u_G}{p_G D_a} \right)^{\frac{1}{3}} \left(a_t d_s \right)^{-2} \tag{7}$$

where:

N_{Re} = Reynolds number (dimensionless) computed as $\frac{L}{a_t u_L}$

N_{Fr} = Froude number (dimensionless) computed as $\frac{L^2 a_t}{p_L^2 g}$

N_{We} = Weber number (dimensionless) computed as $\frac{L^2}{p_1 T_w a_t}$

a_w = wetted area of packing per unit volume (m^2/m^3)

a_t = total surface area of packing material per unit volume (obtained from manufacturer or literature) $(m^2/m^3) k_l$ = liquid-phase mass transfer coefficient (m/sec)

k_g = air-phase transfer coefficient (m/sec)
u_l = viscosity of water (kg-m/sec)
g = acceleration of gravity (9.8 m/sec^2)
p_l = density of water (kg/m^3)
L = liquid flow rate (kg/sec/m^2)
D_w = diffusivity in water (m^2/sec)
d_s = equivalent diameter of sphere with same surface area as a piece of packing material (m)
T_c = critical surface tension of packing material (obtained from manufacturer or from the literature) (kg/sec^2)
T_w = surface tension of water (kg/sec^2)
D_a = diffusivity in air (m^2/sec)
G = gas flow rate (kg/sec/m^2)
u_G = viscosity of air (kg-m/sec)
p_G = density of air (kg/m^3)

Several researchers (Hand et al., 1986; Wallman and Cummins, 1986) have reported good agreement between $K_l a$ values derived from the Onda equations and pilot plant data. In general, the Onda-derived coefficients were somewhat lower than pilot plant data and would result in a conservative design. An important conclusion by Wallman and Cummins (1986) was that $K_l a$ values increase with tower diameter. This trend was attributed to sidewall effects, which were less important as tower diameter increased. Because of this finding, it was predicted that pilot plant determinations of $K_l a$ are also conservative.

Stripping Factor

The stripping factor, R, is a ratio of the actual operating air-water ratio to the theoretical minimum ratio. The theoretical minimum air-water ratio for 100 percent removal is determined by a mass balance in the stripper. It is based on the concept of Henry's law, which states that a certain amount of air must be brought into contact with the water to remove the contaminants. That minimum air-water ratio is described by:

$$\left(\frac{G}{L}\right)_{min} = \left(\frac{C_i - C_e}{C_i}\right)\left(\frac{1}{H}\right) \qquad (8)$$

where

$(G/L)_{min}$ = minimum air-water ratio
H = Henry's constant (dimensionless)
C_i, C_e = concentrations of influent and effluent

As described above, R is the ratio of the actual air-water ratio to this minimum ratio:

$$R = \frac{(G/L)_{actual}}{(G/L)_{min}} \qquad (9)$$

Combining these two equations by substitution, and assuming a given removal efficiency, R can be expressed as:

$$R = (G/L)(H/P_t) \qquad (10)$$

where

P_t = operating pressure (= 1 atm)
H = Henry's constant (atm)

As can be seen, the stripping factor is directly related to the air-water ratio. In turn, these are related to the gas pressure drop through the packed column. There is more than one combination of air-water ratio and air-pressure drop that will achieve a certain removal level. Therefore, these values are iterated to obtain the most cost-effective design (considering both capital and O&M costs). Studies have shown that the most cost-effective stripping factor (on a present-worth basis) usually falls between R = 3 and R = 5 for most gasoline constituents (Hand et al., 1986).

Gas Pressure Drop

The gas pressure drop through the stripping unit is usually determined from a gas pressure drop curve. Many packing vendors will supply a brand-specific pressure drop curve; otherwise, a generalized curve may be used (Figures 21, 22). Using this graph, it is possible to calculate the allowable gas and liquid flow rates for a variety of gas pressure drops. To use the pressure drop curve, find the appropriate value on the x-axis based on the selected air-water ratio. Read up to the chosen gas pressure drop (generally 0.25 to 0.50 in. H_2O per foot is used). It is usually better to use lower pressure drops for lower air-water ratios (CDM, 1986). By reflecting off the curve and reading the corresponding value on the y-axis, it is possible to calculate the allowable gas flow rate from the dimensionless group. Dividing the gas flow rate by the air-water ratio gives the liquid flow rate.

The pressure drop is a function of the gas and liquid flow rates and the size and type of the packing. It is important because it relates to the overall cost of the air stripper and the flexibility of stripper performance. A stripper operating at a high pressure drop will require a smaller volume than a similar stripper at a lower pressure drop. This reduces capital costs for the tower but increases the blower cost, and because the fan will be larger, more power will be required; thus, O&M costs will increase. The various combinations of pressure drops and air-water ratios should be iterated to find the most cost-effective choice. The pressure drop
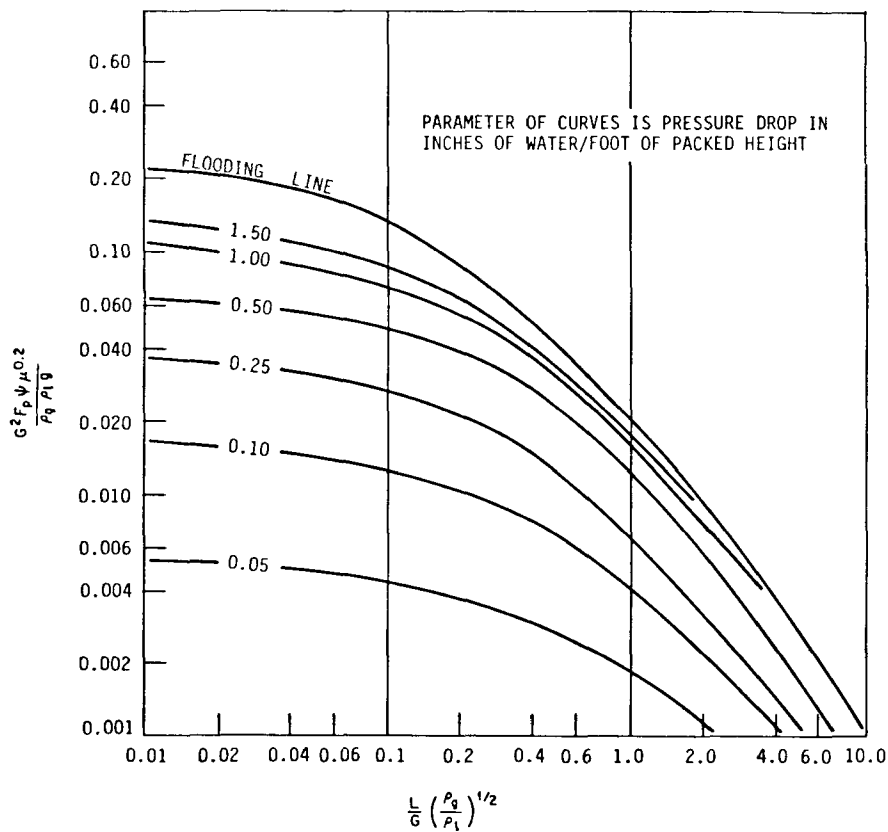
Figure 21. Generalized pressure drop curve for packings (English units).

PARAMETER OF CURVES IS PRESSURE DROP IN INCHES OF WATER/FOOT OF PACKED HEIGHT

FLOODING LINE

1.50
1.00
0.50
0.25
0.10
0.05

$\dfrac{G^2 F_p \psi \mu^{0.2}}{\rho_g \rho_l g}$

$\dfrac{L}{G}\left(\dfrac{\rho_g}{\rho_l}\right)^{1/2}$

Figure 22. Generalized pressure drop curve for packings (metric units).

Approximate flooding

1200
800
400
200
100
50

Gas pressure drop

$\dfrac{N/m^2}{m}$

$\dfrac{\Delta p}{Z}\ \dfrac{lb_f/ft^2}{ft} = 6.37 \times 10^{-3}\ \dfrac{N/m^2}{m}$

$\dfrac{inH_2O}{ft} = 1.224 \times 10^{-3}\ \dfrac{N/m^2}{m}$

$\dfrac{G'^2 C_f \mu_L^{0.1} J}{\rho_G (\rho_L - \rho_G) g_c}$

$\dfrac{L'}{G'}\left(\dfrac{\rho_G}{\rho_L - \rho_G}\right)^{1/2}$
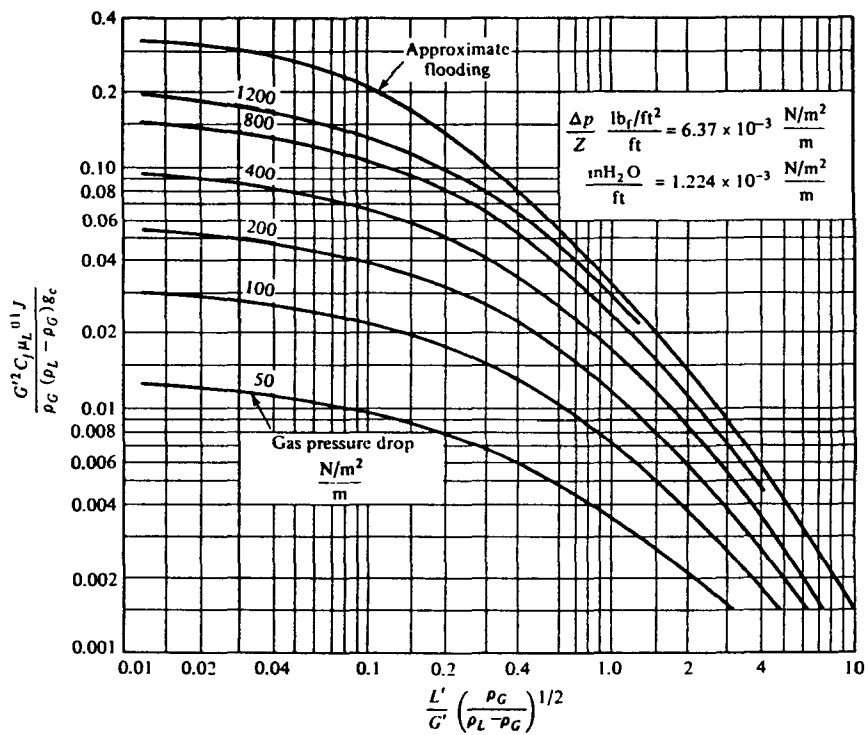
is also important as it relates to tower flexibility. Towers designed and built to operate at a low pressure drop have the flexibility to increase the gas flow rate and hence the air-water ratio, should the future influent concentrations increase or the effluent limitations decrease. This capability will allow higher removal efficiencies and, thus, preserve the current effluent concentrations or allow attainment of stricter limits. Towers designed for high pressure drops do not have this flexibility and would have to decrease the liquid loading to increase the air-water ratio.

The flooding line in Figures 21 and 22 refers to a point at which the stripper no longer functions due to inappropriate air-liquid flow rates. As the gas flow rate is increased (at a constant liquid flow rate), one of a number of changes may occur. These include inversion, by which the liquid is not dispersed; development of a slug of foam; or formation of a layer of liquid at the top of the tower (Treybal, 1980). Above the flooding line, stripping towers do not operate efficiently; operation in this region should be avoided.

Design Equations

After Henry's constant, the mass transfer rate coefficient, the stripping factor, and the gas pressure drop have been determined, all the variables of the master design equation are satisfied. The following equation results from the solution of the mass balance equation:

$$Z_t = \left(\frac{L}{K_1 a}\right)\left(\frac{R}{R-1}\right) \ln \left[\frac{\left(\frac{C_i}{C_e}\right)(R-1)+1}{R}\right] \quad (11)$$

where

Z_t = depth of packing (m)
L = liquid loading rate (m³/m²/sec)
$K_1 a$ = overall liquid mass transfer coefficient (sec⁻¹)
R = stripping factor (dimensionless)
C_i = influent concentration (mg/L)
C_e = effluent concentration desired (mg/L)

This equation gives the total depth of packing necessary to reach the desired flow rate under the stated conditions. This can be thought of conceptually as:

$$Z = (NTU) \bullet (HTU) \quad (12)$$

where

NTU = number of theoretical transfer units

$$= \left(\frac{R}{R-1}\right) \ln \left[\frac{\left(\frac{C_i}{C_e}\right)(R-1)+1}{R}\right] \quad (13)$$

HTU = height of theoretical transfer unit

$$= L/K_1 a \quad (14)$$

NTU is a mathematical expression that characterizes the difficulty of removing a compound from solution. It bears a general relationship to the height of the stripping column. The value of NTU is predominantly influenced by the desired removal efficiency and, to a lesser extent, the stripping factor (air-water ratio).

HTU characterizes the rate of mass transfer from the liquid-phase to the gas-phase. The value is primarily influenced by the mass transfer coefficient and, to a lesser extent, the liquid loading rate. The value bears a general relationship to the tower diameter.

Design Procedure

There is no single procedure that must be followed when designing an air stripping tower. General procedures are suggested in the literature (Kavanaugh and Trussell, 1981; Ball et al., 1984). Regardless of the procedure followed, values are first required for the flow rate, influent and effluent concentration, operating temperature, and the Henry's constant for the limiting contaminant. After these initial values are determined, a suggested general design procedure is:

1. Select the packing material. There are many commercial packings available, each with different mass transfer and pressure drop characteristics. The two broad categories of packing are dumped and stacked (see Removal Efficiencies, p. 70, for a discussion of packing material). A packing should be selected that exhibits a high mass transfer rate with a low gas pressure drop. For water treatment applications, plastic packings are most common because they offer low price, corrosion resistance, and lightweight (2-10 lb/ft³) material that is easily dumped into a tower. Table 15 lists physical characteristics of common packing materials.

2. Select a reasonable stripping factor (between 2 and 10, with 3 to 5 being the best). Calculate the air-water ratio from Equation 10.

3. Refer to Figures 21 and 22. Select a reasonable gas pressure drop. Generally, it is better to choose lower pressure drops (defined as being less than or equal to 100 N/m/m^2) for low air-water ratios. Read graph to find a value for the dimensionless group. Calculate the gas flow rate.

4. Based on the chosen air-water ratio, calculate the required liquid loading rate.

5. Find the tower diameter from $D = \left(\dfrac{4 \ Q\rho_1}{\pi \ L'}\right)^{0.5}$ where Q = flow rate (cfs).

6. Find the height of transfer unit from Equation 14.

7. Find the number of transfer units from Equation 13.

8. Find depth of packing (Equation 12). Use an appropriate safety factor (1.2 is common).

9. Repeat for various values of the stripping factor and gas pressure drop. Determine the most cost-effective combination of parameters based on present worth calculations.

Design Considerations

Several factors should be considered when designing an air stripping tower. One consideration is the character of the area surrounding the air stripper. If the area is residential, the tower, blower, and pumps may need to be enclosed for aesthetic reasons and/or to control noise levels. Depending on various factors (especially the gas flow rate), air strippers can be loud. Zoning laws may also affect stripper design. Many communities have maximum height limitations.

A second consideration would be the prevailing wind patterns of the area. One of the assumptions of air stripping is that the influent air is free of VOCs. In order to ensure this condition, the air intake should be situated in such a manner as to prevent "short-circuiting" between the tower effluent air and influent air. Such a condition would result in lower removal efficiencies.

A third consideration is proper distribution of the influent water throughout the packing. A common problem is channeling along the wall of the tower. Known as "sidewall effect," channeling is caused by the lower flow resistance along the wall, due to a greater void volume. To correct this condition, water is redistributed by side wipers, normally every 20 ft of packing. In general, this problem is more severe with smaller diameter columns.

A fourth consideration is the need for a mist eliminator. This is a device which captures any water entrained in the air before it exits to the atmosphere. These screens are fairly cheap ($200-

$300) and can prevent potentially significant quantities of water from leaving through the top of the column.

A fifth consideration is the effect of influent water quality on the material used for stripper construction. Aluminum is often used for construction because it is not susceptible to rusting. Fiberglass-reinforced plastic (FRP) or stainless steel could be used where water is especially aggressive. Resins used for FRP towers should be potable water/food-grade and have EPA and FDA approval. Carbon steel is generally unacceptable because it tends to rust. If used, the steel should have potable water-grade coating. Concrete is sometimes used.

Other considerations, which include efficiency problems associated with high iron/manganese content of the water and air pollution impacts, are addressed more fully under Limitations, p. 71.

Cost of Air Stripping

One of the main benefits of air stripping as a treatment technology for contaminated groundwater is its general cost-effectiveness compared to other cleanup methods, such as activated carbon. However, the cost of air stripping can vary widely because it depends on many factors and is highly site-specific.

The total cost of any treatment method is a combination of the initial capital costs and the ongoing O&M costs. Capital costs are associated with the startup of the air stripping facility. Included are costs for the process equipment, such as the tower and packing material, air blowers, pumps, piping valves, and electrical equipment; a clearwell and holding tank (if needed); any site-related costs, such as land purchase, bulldozing, and access; vapor-phase control, if required; materials and construction costs for housing, (if required); and miscellaneous costs such as painting, plumbing, and cleanup. Also included in the capital costs are fees for engineering and contingencies, such as legal fees. O&M costs are basically comprised of power for the pumps and blowers and maintenance costs (including labor and materials).

It is sometimes useful to determine the cost of treatment on a volume-treated basis. This is often done to compare the costs at different sites or to compare the costs of different types of treatment. A common expression used is the cost per 1,000 gal treated ($/1,000 gal). This cost represents the marginal cost of treatment. Typical treatment costs on a volume-treated basis are $0.05 to $0.25/1,000 gal.

As described above, the total cost includes both capital and O&M costs. Determining the marginal

O&M costs is fairly easy: divide the costs of power and maintenance for a certain time period by the volume of flow treated in that period. Finding the marginal capital cost is more difficult: estimates must be made for the design life of the facility, the interest rate over that period, and the flow to be treated over the project life. The initial capital costs can then be annualized over the life of the project. Dividing by the estimated yearly flow will yield the marginal capital cost.

Cleanup costs at a particular site are a function of the length of the cleanup, the flow rate to be treated, the desired removal efficiency and/or the final concentration goal, the selected air-water ratio, the physical properties of the limiting contaminant, the residual concentration remaining in the aquifer, conventional water quality parameters, and the need for vapor-phase treatment, among other items. Each of these factors has a particular effect on the overall cost and the marginal cost of treatment. The following paragraphs summarize the various factors and their effects.

Length of Cleanup Time

The length of cleanup time can be one of the most important determinants of both the total and marginal costs. A longer cleanup will usually mean higher initial capital costs but lower marginal costs, because the capital costs can be annualized over a greater number of years. The total operating costs will increase with time, but marginal operating costs are unaffected by the duration of the cleanup.

Flow Rate

The flow rate treated has a direct effect on the costs of treatment. A high flow rate will require a larger tower, clearwell, pumps, and blowers. It will also require more electrical power than a low flow rate. Thus the total capital and O&M costs will increase with the flow treated. The marginal costs, however, will generally decrease as flow rate increases because of economies of scale.

Desired Removal Efficiency

The desired removal efficiency and/or the final effluent goal has a primary influence on the total costs. In general, the higher the desired removal percentage (or the lower the effluent concentration limitation), the higher the capital and O&M costs. More complete contaminant removal (that is, lower effluent concentrations) requires a higher air-water ratio, increased packing depth, or both (all other things being equal). Either factor increases capital costs, and a higher air-water ratio also increases operating costs.

Air-Water Ratio

The air-water ratio is a design parameter chosen on the basis of cost-effectiveness and the Henry's law constant of the limiting contaminant. A higher ratio will increase power requirements but decrease tower volume. The engineer should determine the long-term costs of higher operational costs versus higher initial costs and choose this parameter based on the lowest present-value cost. For aromatic compounds, typical air-water ratios are 20-100:1.

Residual Concentration in the Aquifer

The contaminant concentration allowed to remain in the aquifer is an important cost consideration. As shown in Figure 23, costs are fairly constant for residual aquifer concentrations of 200 to 1,000 ppb (1 ppb = 1 μL) of hydrocarbon. However, as the desired residual concentration approaches the low ppb range, costs increase exponentially. These total costs reflect the need for prolonged pumping life, reinjection of water to flush out the contaminants, and perhaps the use of detergents to loosen contaminants adsorbed to the soil particles. The residual concentration goal should depend on the present danger of the contamination and the future use of the site.

Conventional Parameters

The quality of the water in terms of traditional water quality parameters such as pH, hardness, and iron and manganese may affect the cost of any VOC treatment scheme. Abnormal pH, very hard water, and/or high levels of iron/manganese may require pretreatment of the influent. This could add considerably to the total cost.

Vapor-phase Treatment

If treatment of the stripper off-gas is desired or required, the total cost of stripping can be expected to double (as a rule-of-thumb) (Medlar, 1987). This assumption is based on the use of GAC for treatment and allows for the cost of the initial carbon charge, the contractor, and other site-related and construction costs. Vapor-phase treatment is discussed more fully in Off-Gas Air Pollution Control Systems. As can be seen, many factors influence the cost of air stripping. Because an air stripping tower can reach a certain removal efficiency through a variety of design parameters, an engineer should decide on the most cost-effective combination. To help with this complicated process, several computer cost models have been developed (Nirmalakhandan et al., 1987; Cummins and Westrick, 1982; Clerk et al., 1984). Through the
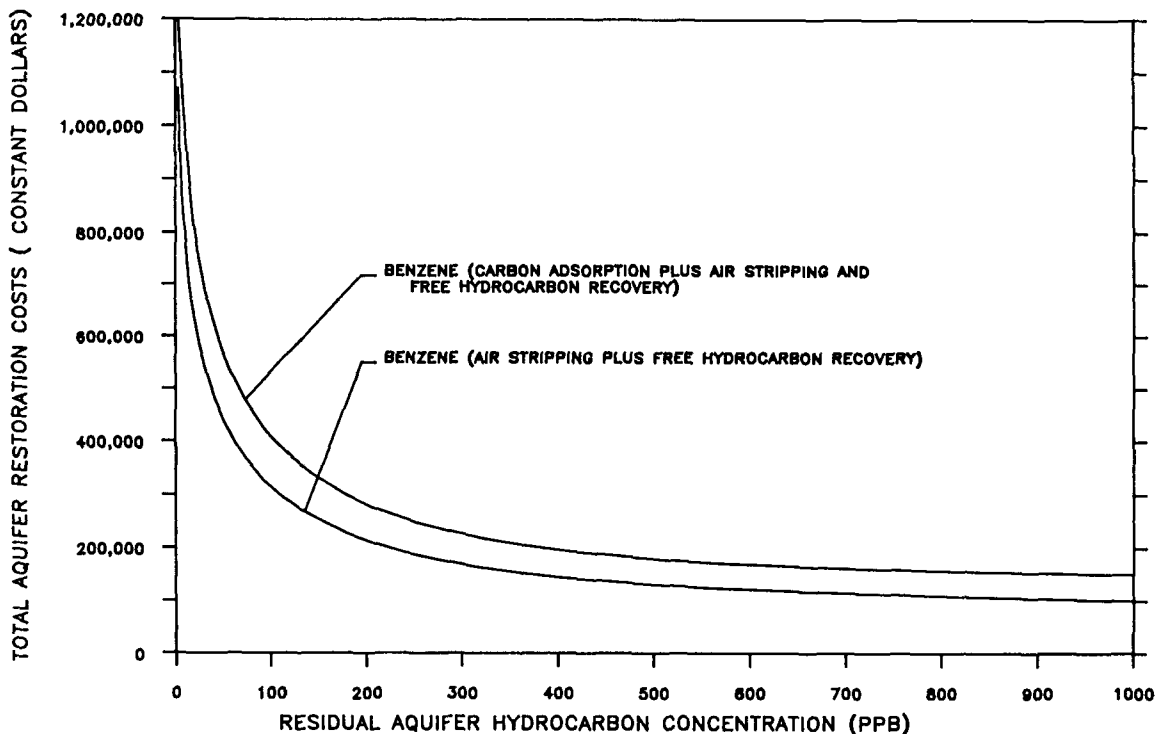
Figure 23. Total cleanup costs as a function of residual aquifer concentration.

use of these models, it is possible to isolate one parameter and optimize costs. For example, two studies optimize cost by iterating the gas pressure drop against the stripping factor, another uses the stripping factor and the liquid loading rate, and a fourth presents cost curves based on liquid flow rates for a variety of alternatives. From these studies, it appears that the most economical stripping factor is between 3 and 5.

To get actual cost figures for this manual, three sources were used: a survey of manufacturers and suppliers of packed tower equipment; case studies from published data which reported cost estimates and after-the-fact costs of cleanups; and cost curves developed by Camp, Dresser & McKee (1987). A survey of tower suppliers resulted in a range of costs from a low of $5,000 (rated to treat 22 gal/min) to $40,000 (rated to treat 450 gal/min). These cost quotes generally include the tower, packing material, mist eliminator, blower fan and motor, and flow meter. The costs depend primarily on the rated flow rate but are also influenced by "extras" such as sampling valves. Because many suppliers custom-design towers for each particular case, their costs varied more widely. Large strippers (rated over 500 gal/min) were generally always custom-built, and thus there are no quoted prices for towers this size. It is assumed that these cost proportionally more than the tower costs quoted above.

The survey of costs from cases reported in the literature yielded a range of capital costs from $27,000 to $1,100,000, and O&M costs from $7,000 to $50,000 annually. According to these reports, the cost of the process equipment (tower, packing, pumps, and fans) accounted for between 20 and 75 percent of the overall capital cost, with higher numbers if air pollution control was required. The fees for engineering and contingencies normally ranged between 20 and 30 percent of the total capital costs. Where necessary, buildings and sitework contributed a significant part of the total cost of the facility (up to 50 percent). The wide range of costs exhibited can be attributed to the factors listed previously, especially the flow rate and whether off-gas pollution control is included. For example, the $27,000 case treated 70 gal/min; the site which cost $1,100,000 included five towers, each 12 ft in diameter and 50 ft high, which combined treated 3,500 gal/min to drinking water levels.

Figures from Camp Dresser & McKee (Figures 24 through 29) give general capital and operating cost estimates for air strippers over a wide range of conditions.

Typical costs for air stripping towers at UST sites are about $130,000 to $150,000 (capital) and $6,000 to $8,000 annual O&M costs.
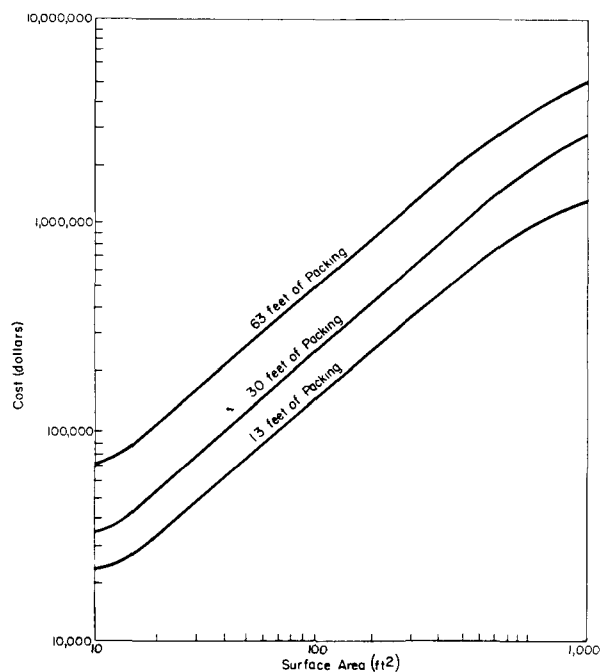
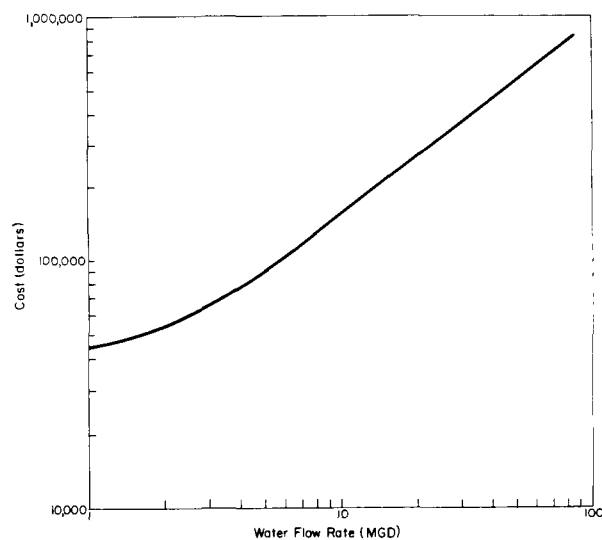**Figure 24. Capital costs for packed tower (based on size).**
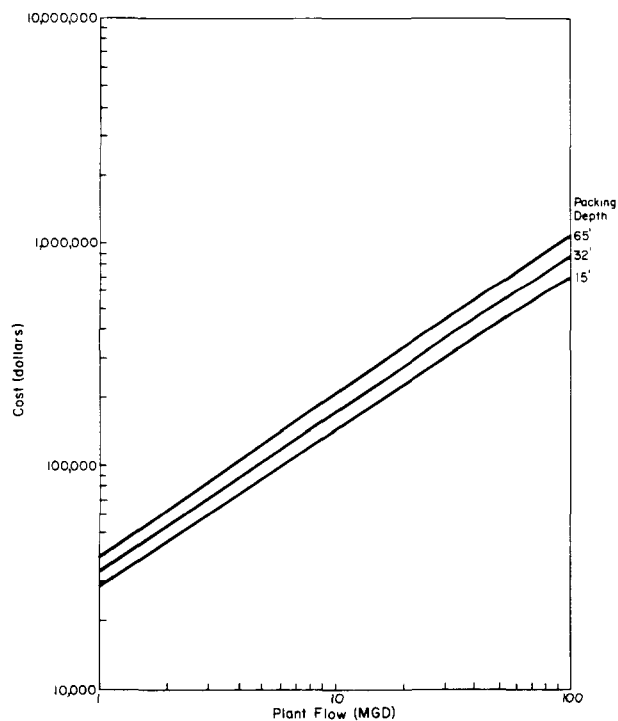

Figure 25. Capital costs for clearwell.
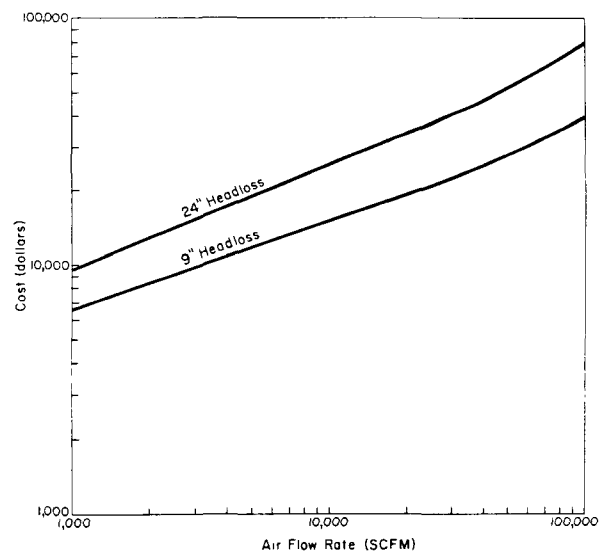

Figure 26. Capital costs for water pump.

Figure 27. Capital costs for air blower (based on pressure drop).
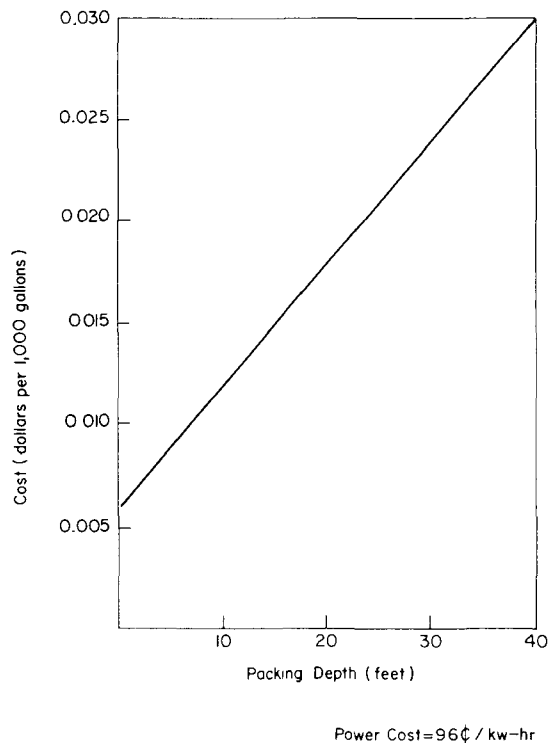
69

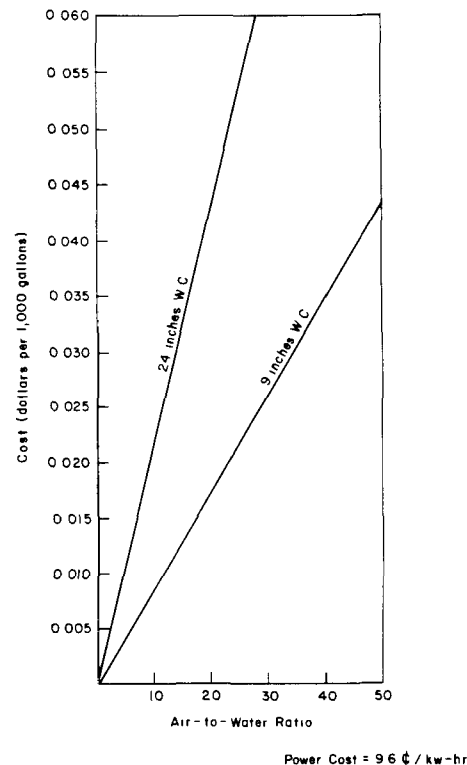**Figure 28. Operating costs for pumping (based on packing depth).**

Figure 29. Operating costs for blower (based on pressure drop).

Removal Efficiencies

The ability of an air stripping tower to reduce VOCs to low levels has been demonstrated in hundreds of pilot-scale and full-scale operations. Like the cost of air stripping, the removal efficiency varies for differing sites and is influenced by a number of factors. Some of these are summarized below.

Water Temperature

The temperature of the influent water significantly affects removal efficiency, as shown in Figure 20, because of the temperature dependence of Henry's constant (see Design Parameters, p. 60). Henry's constant increases with temperature (by about a factor of 1.6 per 10°C increase in temperature), resulting in higher rates of stripping for warmer groundwater. The temperature of groundwater is fairly constant throughout the year at a given location, although it varies in different areas of the country by as much as 15°C. This can have a strong bearing on the success of an air stripping facility.

Influent VOC Concentration

The influent contaminant concentration also affects the percentage removal. For similar conditions, a higher influent concentration will have a higher removal efficiency. This can be explained by recalling that the driving force for mass transfer is proportional to the difference between the operating concentration and the equilibrium concentration of the contaminant. As the operating concentration approaches the equilibrium concentration, the driving force decreases, and relatively less contaminant is removed. For this reason, the final effluent concentration as well as the percentage removal should be considered when designing to achieve a particular effluent goal.

Physical Properties of the Contaminants

Because of their particular Henry's constant, the contaminants to be removed will influence removal efficiency. Compounds with higher Henry's constants can be removed to a higher percentage than those with lower Henry's constants. In cases where multiple VOCs are present, the compound with the lowest Henry's constant will generally be the limiting compound. A compound with a higher Henry's constant at a much higher concentration, however, could be limiting.

Packing Material

The type of packing material can also affect the removal efficiency. The two broad categories of packing are randomly dumped packing and stacked packing. Dumped packing utilizes randomly placed small plastic, metal, or ceramic packings to provide a high surface area and a high void volume. Stacked packing can be described as performing like a bundle of tubes. Dumped packing has been much more common, but stacked packings may offer some advantages. According to manufacturers, stacked packings are less susceptible to biological and mineral fouling due to their higher (in some cases) void space and the fact that stacked packings do not have horizontal surfaces. Table 15 lists physical characteristics of several common dumped and stacked packings.

Air-Water Ratio

Increasing the air-water ratio will usually result in increased removal efficiency. However, this effect may have diminishing marginal returns (Hand et al., 1986). For most gasoline compounds, very high-level removal (99+%) requires a very high air-water ratio.

Data from full-scale operations have shown that of 95 to 99 percent of the influent concentration of VOCs can normally be removed. In some cases in fact, the product water is used for drinking water. Air stripping is most effective for removing low-molecular-weight, nonpolar compounds with low solubilities; benzene, toluene, xylene, and other aromatics are normally removed to very low levels.

It is important to realize that the removal efficiency of an air stripping tower is fixed by the design and will not change over the life of the cleanup (assuming initial conditions do not change). This differs from the use of activated carbon, whose removal effectiveness depends on the life of the carbon and generally decreases over time for each carbon change.

Ease of Operation

One of the main advantages of air stripping is its relative ease of operation. Once the tower, blower, pumps, valves, electrical instrumentation, and appurtenances are in place and operating, the facility is practically self-operating. There is no recurring maintenance (such as carbon replacement) that requires the services of an engineer beyond normal maintenance. Iron and manganese or biological interferences could cause operational problems, however, which would require the services of an engineer.

Reliability

The ability of air stripping to consistently produce high-level removal efficiencies for volatile groundwater contaminants is well documented. In the past, removal to low ppb levels or to below-minimum-detection levels of benzene, toluene, and xylene has normally been achieved. Each site has its own characteristics and problems, however, and complicating factors may prevent the achievement of such low levels at every site. The more conservative designs may add a safety margin for low-level removals.

Limitations

The use of air stripping for the removal of dissolved gasoline from groundwater may be limited by several factors. These include the types of chemicals which can be removed effectively by air stripping; possible air pollution impacts of the stripping tower effluent; high iron and manganese and/or suspended solids concentrations in the influent water; and possible high noise levels from the stripper.

Perhaps the most important limitation of air stripping is that many types of groundwater contaminants cannot be removed by this method. It is applicable only to the removal of volatile compounds. The major constituents of interest in gasoline, such as benzene, toluene, xylene, and ethylbenzene, are all fairly volatile and thus easily removed. Compounds with low volatility, such as 1,2-dichloroethane (EDC), are not readily removed by this technique. In general, very soluble compounds, high-polarity compounds, and high-molecular-weight compounds are not easily removed by stripping.

The possibility of air pollution from the gaseous effluent from air stripping towers has caused concern. The operation of a stripping tower does not destroy the contaminant; it simply transfers the contaminant from the liquid to the gaseous phase. It is assumed that through the dilution occurring in the tower and the mixing in the atmosphere, the ambient concentration of the contaminant entering the atmosphere will be below safe levels. New Jersey, California, and Michigan have regulations that limit the discharge of volatiles to the atmosphere. In New Jersey, no source is permitted to discharge more than 0.1 lb/h of any particular VOC, including benzene. For strippers exceeding this limit, off-gas air pollution control is required. Typically, carbon

Table 15
Physical Characteristics of Common Packing Materials

Dumped Packings

Type	Size (in.)	Surface Area (sf/cf)	Void Space (%)	Packing Factor[2] (1/ft)
Glitsch	OA	106	89	60
Mini-Rings	1A	60.3	92	30
(Plastic)	1	44	94	28
	2A	41	94	28
	2	29.5	95	15
	3A	24	95.5	12
Tellerettes	1" (#1)	55	87	40
(Plastic)	2" (2-R)	38	93	18
	3" (3-R)	30	92	16
	3" (2-K)	28	95	12
Intalox	1"	63	91	33
Saddles	2"	33	93	21
(Plastic)	3"	27	94	16
Pall Rings	5/8"	104	87	97
(Plastic)	1"	63	90	52
	1½"	39	91	40
	2"	31	92	25
	3½"	26	92	16
Raschig Rings	½"	111	63	580
(Ceramic)	¾"	80	63	255
	1"	58	73	155
	1½"	38	71	95
	2"	28	74	65
	3"	19	78	37
Jaegar	1"	85	90	28
Tri-Packs	2"	48	93	16
(Plastic)	3½"	38	95	12

Stacked Packing

Type	Size (in.)	Surface Area (sf/cf)	Void Space (%)	Packing Factor[2] (1/ft)
Delta (PVC)	—	90	98	—
Flexipac	Type 1	170	91	33
(Plastic)	Type 2	75	93	22
	Type 3	41	96	16
	Type 4	21	98	9

[1]Taken from manufacturers' data and Treybal (1980)

[2]Represents "typical" value; actually a variable.

adsorption is used to treat the vapor-phase contaminant. Figure 30 shows the amount of a particular volatile or total volatiles which would be released to the air at the stated flow rates and removal efficiencies. (It is interesting to note that at gas stations, VOC discharges of 10 lb/h have been measured.)

Another limitation of air stripping may be high noise levels resulting from tower operation. If the facility is in a residential neighborhood, the noise could be very disturbing, especially if the tower is being operated at a high gas loading rate. One solution is to surround the tower with walls extending above the tower.

High concentrations of iron and manganese and/or suspended solids in the influent water can limit the effectiveness of air stripping. Iron and manganese facilitate the growth of bacteria on the packing, causing decreased mass transfer rates and higher gas pressure drops. The presence of toluene in the influent is thought to contribute to this effect (Abrams, 1987). Suspended solids can cause similar problems if they are trapped by the packing. Many methods have been used to remediate pack-

ings clogged with iron hydroxides or biological fouling. Some facilities remove the packing and physically remove attached growth. Normally, however, a rinse of some type is used. According to Jarnis et al. (1987), a strong chlorine or hydrogen peroxide rinse can be used for biological fouling, while a dilute acid rinse may be used for iron hydroxide clogging. Stacked packings appear to have less of a tendency to clog because they do not have any horizontal surfaces on which bacteria/hydroxides can gather.

Off-Gas Air Pollution Control Systems

Possible air pollution from the operation of stripping towers is a major concern in some areas and is a potential limiting factor for the use of this treatment technique. In cases where treatment of the stripper off-gas is desired or required, vapor-phase GAC is the most common treatment. This method transfers the contaminant onto the GAC after it has volatilized from the liquid. Other treatment methods include incineration and catalytic oxidation.

The advantage of using vapor-phase GAC after a stripper (as compared to using liquid-phase GAC and foregoing the stripper) is in the greatly
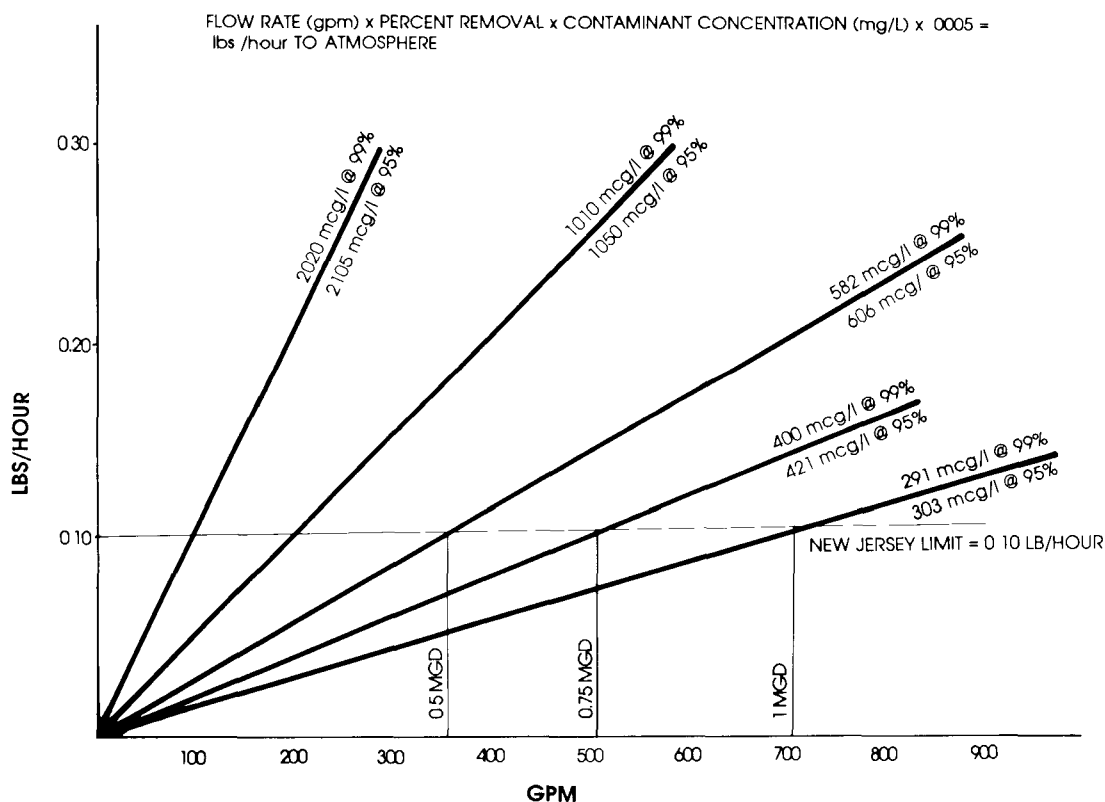

Figure 30. Representative volatile organic compound discharge rates.

increased adsorption capacity of the GAC in the vapor-phase. By transferring the contamination to the vapor-phase (via air stripping) prior to removal by GAC, the carbon can adsorb much more contaminant and therefore will last much longer; thus O&M costs are significantly reduced. For example, Zanitsch (1979) reported a vapor-phase adsorption capacity for toluene of 26 percent by weight (260 mg/g). This compares favorably with a liquid-phase capacity of 2.6 percent (26 mg/g) (Dobbs and Cohen, 1980). Depending on the chemical in question, the vapor-phase adsorption capacity can be from 3 to 20 times higher than the liquid-phase capacity (Medlar, 1987).

In order for vapor-phase GAC to be properly utilized, the off-gas relative humidity must be reduced to below 50 percent. This can be done by using desiccants or heating the air. If the relative humidity is not reduced, the capacity of the carbon is significantly reduced because the water molecules occupy adsorption sites preferentially. Another consideration in the design of a vapor-phase GAC system is the approach velocity: it must be kept below 100 ft/min for effective adsorption.

The cost for vapor-phase GAC systems is typically $100,000 for single tank (bed) units and $120,000 for dual tank units (CDM, 1987). These costs do not include the cost of the carbon or the operational cost. These costs are fairly constant over a range of treatment sites. Table 16 gives approximate relative cost ranges for several treatment alternatives.

Table 16
Relative Cost Factors for Treatment of Groundwater

Technique	Relative Cost Factors[1] Capital	O&M	O&M (RCRA)[2]
Air stripping	1*	1*	1
Air stripping & vapor-phase GAC	2.0	3.0	4.0
Air stripping & liquid-phase GAC	3.0	3 0	4.5
Air stripping & liquid-phase & vapor-phase GAC	4.0	5.0	7.5
Liquid GAC only	1.5	4.0	8.0

Source: CDM, 1987.

*Assigned
[1] Cost factors indicated are relative to air stripping.
[2] Indicates cost if spent carbon must be treated as a hazardous waste under RCRA.

Activated Carbon Adsorption

Background

Carbon has been used as an adsorbent for centuries; the ancient Hindus reportedly filtered their water with charcoal (Cheremisinoff and Ellerbusch, 1978). The beverage industry has used GAC for water treatment since the 1930s. In the mid-1960s increasingly large numbers of municipal water treatment facilities began choosing GAC to control taste and odor problems (Bright and Stenzel, 1985). Because GAC has the ability to remove a large variety of compounds (including organics) from water, its use has increased greatly over the past 20 years as a treatment for organic contamination of surface waters and groundwaters. Today, along with air stripping, it is one of the most common methods for treating groundwater contaminated by VOCs, including gasoline.

Activated carbon can be either powdered (PAC) or granular (GAC). Powdered carbon refers to particles that are smaller than U.S. Sieve Series No. 50; granular carbon is anything larger than this (Cheremisinoff and Ellerbusch, 1978). PAC is generally not recoverable in usable form. It is normally used as part of a treatment train, where it is added to the water and later removed by sedimentation or coagulation. Thus, PAC use is limited to complete treatment systems, in which the product water is to be used for drinking water. Since most leaking UST sites will not require extended treatment trains, GAC is the usual choice when activated carbon is to be used. The GAC is normally recovered for reuse.

Adsorption Processes

Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Either chemical or physical forces cause the molecules to collect on the solid. Whether chemical or physical, adsorption occurs when the attractive forces at the carbon surface overcome the attractive forces of the liquid. Chemical adsorption is said to have occurred when the attraction is so strong at the carbon surface that a chemical compound is formed. Physical adsorption is due to van der Waals' forces, which in comparison to chemical adsorption, are extremely weak bonds. In environmental engineering applications, adsorption usually refers to physical adsorption.

Van der Waals' forces are common to all matter and are thought to be the result of the motion of

electrons. Molecules held by van der Waals' forces are weakly adsorbed and can be removed by changing the solute concentration or by adding enough energy to overcome the bonds. This ability to remove certain molecules adsorbed on carbon and to reuse the carbon several times is what allows GAC adsorption to be a cost-effective technology.

The mass transfer of a solute from the bulk liquid to the carbon surface has three basic phases (Figure 31). First, bulk transport carries the solute (contaminant) among the carbon particles themselves. This type of transport is affected by the type of carbon and the liquid velocity. Second, film transport occurs as the solute diffuses from the bulk liquid across the theoretical hydrodynamic layer surrounding the carbon particle. The rate of mass transfer across this layer is assumed to depend on the mass transfer coefficient k (Perry and Chilton, 1973). Third, the particle undergoes intraparticle transport throughout the carbon pores. This step can be divided further into pore diffusion, surface diffusion, and micropore diffusion. The internal pores of activated carbon are classified, based on their size as micropores (10-1000 Å) or macropores (over 1000 Å) (Cheremisinoff and Ellerbusch, 1978). Pore diffusion describes the process whereby the solute is transported into and through the macropores. The only reaction that occurs is adsorption on the macropore walls. Surface diffusion occurs when particles already adsorbed on the pore walls move further into the carbon particle. Micropore diffusion is the transport mechanism by which the adsorbate is carried into the micropores where it reacts with the carbon walls.
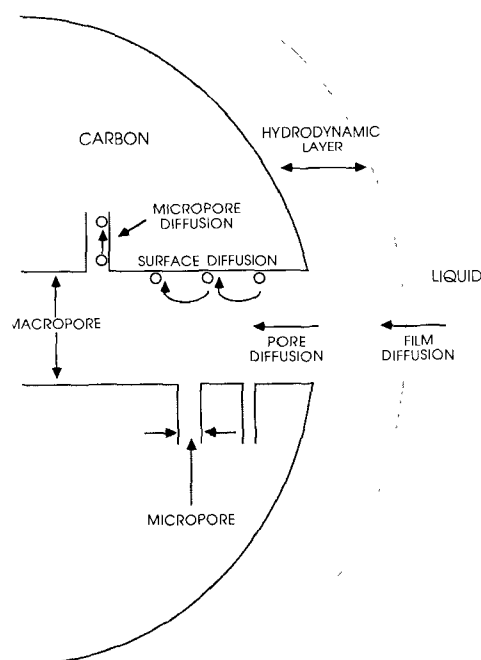

Figure 31. Mass transfer of solute from liquid to carbon particle.

Activated Carbon as an Adsorbent

Activated carbon is used as an adsorbent because of its large surface area, a critical factor in the adsorption process. The typical range for surface areas of commercially available activated carbon is 1,000 to 1,400 m^2/g. This very large surface area results from the unique internal pore structure of activated carbon (Figure 32). Most of the available surface area is internal.
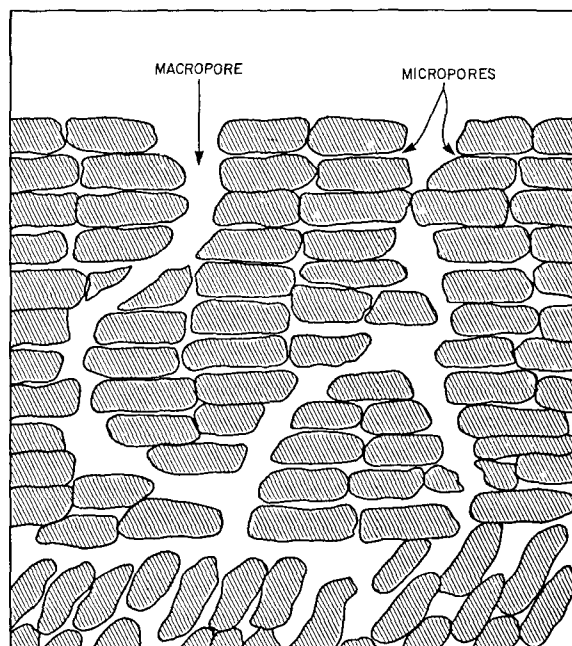

Figure 32. Idealized diagram of internal pore structure of GAC.

Activated carbon is a general term that refers to a group of substances. It originates from several different sources, including bituminous coal, coconut shells, lignite, wood, tire scrap, and pulp residues, with coal being the most common. To form GAC, the particular base is subjected to three steps: dehydration, carbonization, and activation. The dehydration step removes water by heating the material to 170°C. Further increasing the temperature drives off other vapors (CO_2, CO, CH_3COOH) and decomposition begins, resulting in carbonization. Activation occurs when superheated steam is released into the system, enlarging the pores by removing the ashes produced during the carbonization step.

GAC Evaluation: The Isotherm

The basic instrument for the evaluation of activated carbon treatment is the adsorption isotherm. The isotherm is a function that relates the amount of solute adsorbed per weight of adsorbent to the solute concentration remaining in the liquid at equilib-

rium. As the term implies, isotherms are temperature-dependent, so values are given in terms of temperature. The isotherm function (shown in Figure 33) can be thought of as a means of describing the capacity of carbon for a particular compound, or the efficiency of carbon to remove that compound.
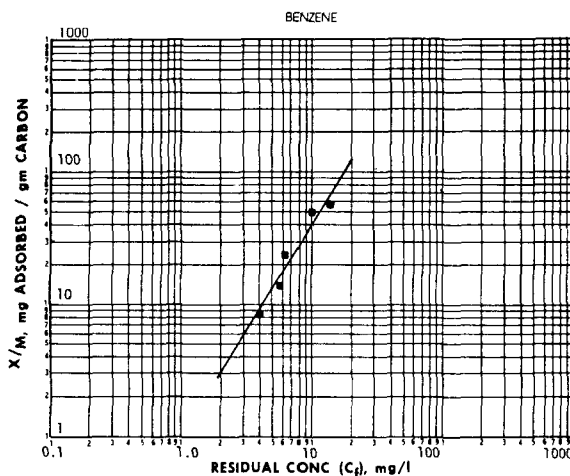

Figure 33. Freundlich isotherm for benzene.

The carbon capacity is influenced by a variety of factors: the solute to be adsorbed, the adsorbent (carbon) itself, the water temperature, the pH of the liquid, and other things. Isotherms are usually determined for a single-solute solution. If more than one compound is present in the water, as is usually the case at gasoline contamination sites, the isotherms are useful only for comparative purpose, not for design purposes.

The equations most commonly used to describe experimental isotherm data are those by Freundlich and Langmuir (see Figure 33). The Langmuir isotherm is of the form:

$$\frac{X}{M} = \frac{QbC}{1+bC} \qquad (15)$$

where

X/M = amount of adsorbate (X) per weight of adsorbent (M)

Q = amount of adsorption per unit weight forming a complete monolayer

C = concentration of solute in water at equilibrium

b = $b_0 exp(-E/RT)$

where

b_0 = a constant that includes the entropy term
E = energy of adsorption
R = universal gas constant
T = absolute temperature (°K)

The Langmuir isotherm equation was developed theoretically to closely model the adsorption process, as evidenced by the term Q, which assumes that a monolayer forms on the carbon. The more commonly used Freundlich isotherm, on the other hand, represents an empirical equation. It has the general form:

$$X/M = KC^{1/n} \qquad (16)$$

where

X/M = amount of adsorbate per weight of adsorbent

C = concentration of solute in water at equilibrium

K,n = empirical constants specific to the compound

The empirical constants, K and n, are determined by plotting experimental results, with the amount of solute adsorbed on the y-axis and the equilibrium solution concentration on the x-axis. The isotherm is typically linear. The slope of the line is equal 1/n, while the y-intercept is equal to K. Although the constants have no physical significance, they are useful for comparing the adsorption capacities of different compounds or for the same compound on different carbons. Isotherms are specific to the type of carbon used.) Values for these parameters are commonly found in the literature. Table 17 summarizes reported K values, representing carbon capacities for some gasoline components.

Activated Carbon Life and Breakthrough

Within an operating carbon tank, three distinct zones are present (Figure 34). The equilibrium zone, located at the influent end of the tank, is the area where the carbon is saturated with contaminant. At the downstream end of the carbon tank is an area where the carbon retains its complete adsorptive capacity. Between these two zones is

Table 17
Carbon Adsorption Capacities for Selected Compounds

Compound	Adsorption Capacity (mg/gr)	Reference
Vinyl Chloride	Trace	Nyer, 1987
Methylene Chloride	Avg: 1.2	
	1.3	[1]CDM, 1987
	1.6	[2]CDM, 1987
	0.8	Nyer, 1985
	1.3	Dobbs & Cohen, 1980
1,2-Dichloroethane (EDC)[1]	Avg: 2.5	
	3.6	Dobbs & Cohen, 1980
	2.0	Nyer, 1985
	3.6	Hall & Mumford, 1987
	0 3	Hall & Mumford, 1987
Benzene[1]	Avg: 16	
	1.0	Dobbs & Cohen, 1980
	27.4	CDM, 1987
	80	Verschueren, 1977
	4.1	Hall & Mumford, 1987
	1.73	Hall & Mumford, 1987
Ethylene Dibromide (EDB)[1]	Avg 17.0	
	17.0	Neulight, 1987
Toluene[1]	Avg: 22.5	
	26	Dobbs & Cohen, 1980
	50	Verschueren, 1977
	2	Hall & Mumford, 1987
	12	Hall & Mumford, 1987
Ethylbenzene[1]	Avg: 24	
	53	Dobbs & Cohen, 1980
	18	Verschueren, 1977
	2.2	Hall & Mumford, 1987
p-Xylene	Avg: 46	
	85	Dobbs & Cohen, 1980
	55	Hall & Mumford, 1987
	50	Hall & Mumford, 1987
	28	Bright & Stenzel, 1985
	13	Bright & Stenzel, 1985
Naphthalene[1]	Avg. 68	
	132	Dobbs & Cohen, 1980
	5.6	Nyer, 1985
Phenol[1]	Avg: 91	
	161	Verschueren, 1977
	22	Dobbs & Cohen, 1980
bis (2-Ethylhexyl) phthalate	11,300	Dobbs & Cohen, 1980

[1]Gasoline Components

INFLUENT

EQUILIBRIUM ZONE
(ZONE OF EXHAUSTION)

BED
DEPTH

MASS TRANSFER ZONE
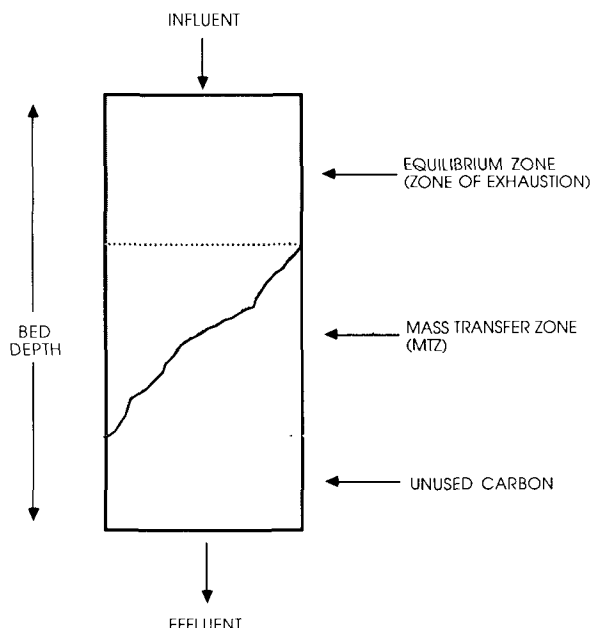(MTZ)

UNUSED CARBON

EFFLUENT

Figure 34. Idealized diagram of zones within GAC reactor.

the mass transfer zone (MTZ), where adsorption is taking place. Within the MTZ, a concentration gradient develops, with a high concentration at the influent end of the MTZ decreasing to near-zero concentrations for most contaminants at the downstream end of the MTZ. The length of this MTZ depends on the loading rate and the characteristics of the adsorbent and adsorbate. The total length of the MTZ represents the resistance to adsorption.

The MTZ moves downward through the column as the total volume of water treated increases. Eventually, the leading edge of the MTZ reaches the end of the column (Figure 35), and the effluent contains increasingly higher concentrations of contamination as time passes. When the effluent concentration reaches a given concentration (determined arbitrarily or based on effluent standards), breakthrough is said to have occurred, and the carbon is normally replaced. Figure 36 shows an idealized breakthrough curve. The breakthrough characteristics are an important determinant in deciding whether GAC is appropriate for a particular site. Breakthrough is discussed in more detail on p. 81.

Design of Carbon Systems

The design of an activated carbon system is not as straightforward as the design of an air stripping tower. Rather than the basic equations that are

used to determine the size and operating parameters of a stripping tower, design of a GAC system requires more complete pilot testing and engineering judgment. The adsorption characteristics of any particular combination of contaminants are not generally predictable, except in a few situations where certain common chemicals are found and the engineer has vast experience. Even under these conditions, a pilot test using the water of interest is often required to forecast accurately the optimal empty bed contact time (EBCT) and carbon usage rate at a specific site.

When designing a GAC system, the EBCT is chosen first. The EBCT is defined as the volume of carbon divided by the flow rate. The EBCT relates directly to the size of the contactor needed; a high EBCT requires more carbon. The EBCT is inversely related to the carbon usage rate; the higher the EBCT, the lower the usage rate. The goal of the GAC system design is to find the optimal point in the tradeoff between a lower carbon usage rate and a smaller contactor size. A typically used minimum EBCT for gasoline spills is 15 min. For a standard 20,000-lb supply of carbon in a 10-ft diameter column, this EBCT results in a liquid loading rate of 2 gal/min per ft^2. Experience has shown that this configuration results in a system with a good removal rate and high flexibility, should future conditions change (Neulight, 1987).
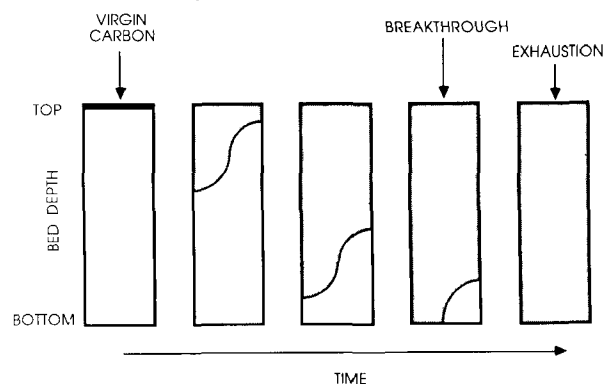

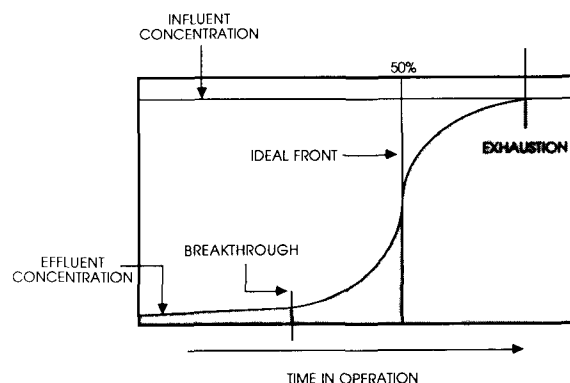Figure 35. Breakthrough and exhaustion in an operating GAC reactor.

Figure 36. Idealized single-solute breakthrough curve.

78

The second design variable is the decision to use a single-stage or multistage operation (discussed below in Operation of Carbon Systems). This decision is based on the breakthrough characteristics of the influent stream, as well as financial considerations. Influents that exhibit a long MTZ are better operated in a multistage fashion (Figure 37) because this mode allows more efficient use of the carbon, although at a higher overall cost.
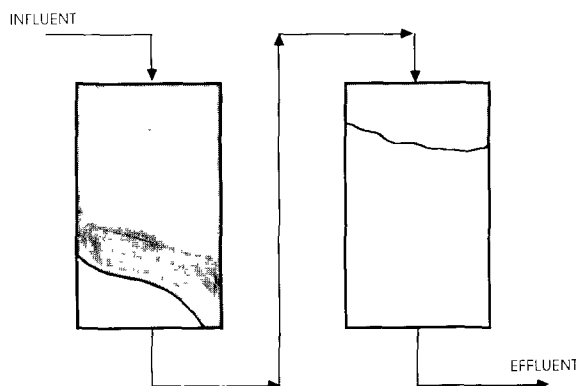

INFLUENT

EFFLUENT

Figure 37. Schematic diagram of multistage GAC contactors.

Operation of Carbon Systems

Facilities using GAC at leaking UST sites are normally operated as fixed bed facilities. The contactors may be either gravity or pressure filters and may be single-stage or multistage. Each choice offers benefits for specific conditions.

Fixed-bed columns may employ upflow or downflow of the liquid. If downflow is used, the carbon bed acts as a filter for suspended solids in addition to removing organics. Filtering may be undesirable in some cases (for example, where the suspended solids concentration is high) because of the high head losses which result and extra backwashing that is necessary. In these cases, upflow of the water would be preferred.

Gravity GAC filters are usually made of concrete and are operated similarly to sand filters. They are generally used for very high flows, such as are common at municipal water treatment plants (1 to 5 million gallons per day). Gravity filters are not used at most leaking UST sites. Rather, pressure filters are used because they allow higher surface loading rates (5 to 7 gal/min per ft^2) than do gravity filters at 2 to 4 gal/min per ft^2; and they also pressure-discharge, which saves repumping costs. They are limited to diameters of 12 ft or less, sizes in which the cylinders are normally available. They are typically 10 ft in diameter. A vessel 10 ft in diameter and 10 ft high holds approximately 20,000 lb of carbon. When wet, this amount weighs about

40,000 lb, which is the maximum allowable weight that can be shipped on U.S. highways and thus determines the typical size for carbon filters.

GAC contactors may be operated either as single-stage or multistage. In multistage use (Figure 37), the leading contactor removes the majority of the contamination, while the second contactor acts as a "polishing" step, removing any residual organics from the water. In series operation, the entire adsorptive capacity of the carbon is used. The lead contactor can be used past breakthrough (i.e., to exhaustion) because the second contactor continues to remove the constituents. After the spent carbon is replaced, the piping is reversed so that the new carbon becomes the polishing bed. Multistage operation is the optimal use of carbon. The cost for this method, however, is higher than single-stage and may not always be justified, especially where discharge limitations are not stringent.

Removal Efficiency

Many case studies have demonstrated the ability of activated carbon to remove a variety of compounds in gasoline to nondetectable levels (99.99 + % removal). The effectiveness of GAC at a particular location depends on several factors, but primarily on the compounds to be removed. The appropriateness of GAC for a site depends primarily on cost and how it is influenced by factors such as influent concentrations, effluent use (concentration limits), composition of the groundwater, and available alternatives to GAC treatment. For example, GAC can almost always reduce gasoline-contaminated groundwater to less than 1 ppb of benzene. However, in cases where the influent concentration is very high, and/or the discharge requirements are not strict, air stripping (either alone or prior to GAC) may be a more cost-effective and appropriate means of removing the benzene. The following paragraphs summarize the factors that influence the choice of GAC for groundwater remediation.

Effectiveness

Although activated carbon has been used successfully to remove many gasoline compounds from water, not every compound can be removed. GAC works best for low-solubility, high-molecular weight, nonpolar, branched compounds (Bourdeau, 1987). According to Brunotts et al. (1983), a compound's solubility in water is the key parameter in determining how well it will adsorb. Low-solubility compounds are adsorbed better than high-solubility compounds, all other things being equal. For this reason, alcohols, ketones, and ethers are poor adsorbers, whereas most solvents and pesticides are excellent adsorbers. High molecular weight compounds adsorb better than low molecular

weight compounds, perhaps because of their higher van der Waals' forces. Extremely high molecular weight compounds, such as sugars, however, do not adsorb at all, but these compounds are not usually found in groundwater.

GAC has a higher affinity for nonpolar compounds than for polar compounds due to the surface chemistry of the carbon. The polarity of a compound depends on the chemical and physical structure of its molecules. Polar compounds behave more like ionic compounds, while nonpolar compounds are more neutral electrically. Most components of gasoline, particularly benzene, toluene, and xylene, are nonpolar. The molecular structure of a compound will also influence its ability to adsorb on GAC. Molecules which are branched or have attached functional groups, such as chlorine, fluorine, or nitrogen, adsorb well. Pesticides generally exhibit extremely high adsorbability, due in part to their complex molecular structure.

Other factors also influence the effectiveness of GAC treatment: properties of the carbon product itself, temperature of the water, iron and manganese concentration of the water, the EBCT, desorption, and bacteria activity.

As discussed earlier, GAC originates from several different materials and can be prepared by a variety of methods. For these reasons, different GAC products have different adsorptive capacities. The surface area of the carbon is the most important factor in determining its efficiency, because the amount of adsorption is directly proportional to this value. The surface chemistry of various carbons differs also, but this effect is minor compared to that of surface area. Regenerated carbon also differs from virgin (unused) carbon. According to Bourdeau (1987), virgin carbon is normally used in cases where the effluent is to be used for drinking purposes. Reactivated carbon, which costs significantly less, is normally acceptable for sites where the effluent is discharged to surface or groundwater.

The temperature of the water also affects adsorption (Snoeyink, 1983). As the temperature increases, adsorptive capacity decreases. The effect of temperature in groundwater cases is minimal, as the groundwater temperature in a given locale is fairly constant throughout the year.

Groundwaters containing significant (above 5 mg/L) levels of iron and manganese must be treated to remove these compounds before GAC treatment. If the iron and manganese are not removed prior to GAC treatment, they will precipitate onto the carbon, clog the carbon pores, cause rapid head loss, and eventually prevent flow through the carbon.

As stated above, the volume of GAC divided by the flow rate to the column is defined as the empty bed

contact time (EBCT). It represents the theoretical time that the GAC is in contact with the water; however, the actual time of contact is about half of the EBCT because the interparticle porosity of GAC is roughly 50 percent. The optimum EBCT is unique to each facility. It depends on the type of carbon used, contaminants being removed, bed depth, flow rate, and influent and effluent concentrations. Values for EBCT reported in the literature vary widely, from 3 min to 2,000 min, certainly a reflection of the variety of situations to which GAC has been applied. A typically used minimum EBCT for gasoline compounds is 15 min, which corresponds to a surface loading rate of 2 gal/min per ft^2. Where the compounds present are more difficult to adsorb, a 30-min minimum EBCT is used. To determine the optimum EBCT for a particular site, pilot studies can be used.

Desorption is the reverse of adsorption. Desorption may occur with a sudden decrease in the influent concentration. If this occurs, previously adsorbed contaminant molecules may desorb so that equilibrium in the solution is maintained. This can result in an effluent concentration that is higher than the influent concentration. The phenomenon of displacement may also occur if more strongly adsorbable contaminants appear in the influent and displace the previously adsorbed compounds (Figure 38). This also results in higher concentrations of those compounds in the effluent than in the influent.

GAC beds are excellent media to support biological growth. Once there, the bacteria are able to degrade certain compounds from the bulk liquid and the surface of the GAC (Speital and DiGiano, 1987). The occurrence of biodegradation has several benefits. Perhaps the most important benefit is the increased service life of the carbon. Compounds that are degraded do not occupy sorption sites, so those sites are available for other molecules. Speital and DiGiano found that a reservoir of empty sorption sites may serve to dampen variations in the effluent, preventing higher effluent concentrations resulting from increased influent concentrations. Van der Kooij (1983) discussed possible negative aspects of biological growth on GAC, including the formation of endotoxins, high colony counts, and possible anaerobic conditions.

Appropriateness of Using GAC

After determining whether GAC could effectively remove the contaminants of concern at a leaking UST site, the most cost-effective technique must be determined. The decision whether this is GAC will be based on the primary factors affecting cost: influent concentrations of the contaminant(s) and total organic carbon (TOC); desired effluent con-
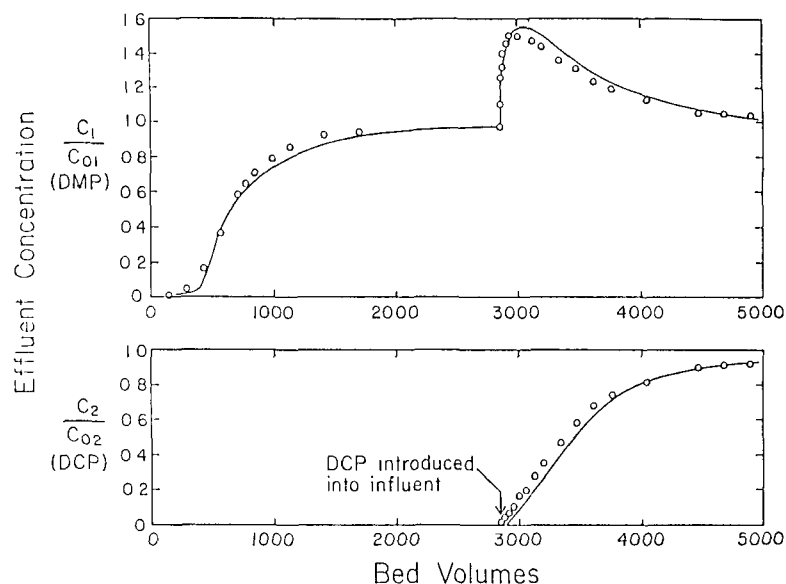
Figure 38. Displacement from GAC of dimethylphenol (DMP) by more strongly absordable dichlorophenol (DCP).

centration; and breakthrough characteristics of the contaminants in the influent.

GAC is best suited for reducing low influent gasoline concentrations to nondetectable levels. In situations where the influent concentration of TOC is high, the carbon usage rates increase dramatically. O'Brien and Fisher (1983) report the results of 31 contamination case studies (not all gasoline-related, however) in which GAC was used. In 17 cases where the influent TOC was above 1 mg/L (1,000 ppb), the median carbon usage rate was 1.54 lb/1,000 gal treated. For the 14 cases where influent TOC was below 1,000 ppb, the median carbon usage rate was 0.35 lb/1,000 gal. It can be seen that treating a high influent concentration uses much more carbon and is therefore significantly more expensive than treating a low influent concentration.

Carbon is well suited to remove most gasoline contaminants to nondetectable levels. It is therefore an excellent choice where effluent standards are stringent, such as drinking water standards. Unlike air stripping, which has a specific percentage removal of less than 100 percent, carbon can remove compounds to nondetectable limits prior to breakthrough.

Waters with many contaminants, such as gasoline-contaminated waters will increase the carbon usage rate significantly. This is due to competitive adsorption. Conceptually, carbon has a limited number of adsorption sites. Each site can accommodate one molecule; once the site is filled, no other molecules are able to adsorb there. An influent with many compounds will have a carbon usage rate between that predicted by the com-
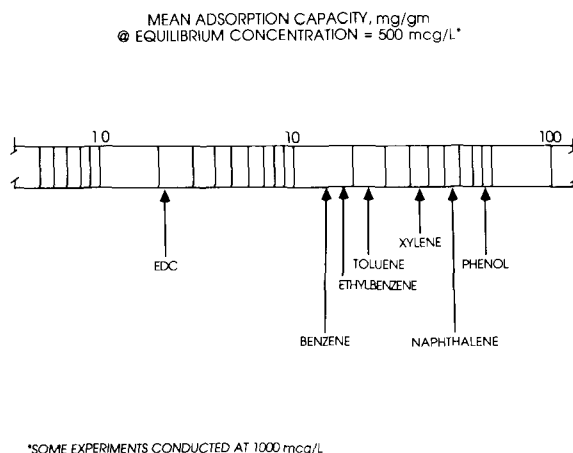
pound of earliest breakthrough and that predicted by the sum of the usage rates of the individual compounds (Hall and Mumford, 1987). In some cases of competitive adsorption, displacement may occur if a more strongly adsorbable compound is introduced into the contaminant stream.

The breakthrough characteristics for each influent stream are also important in determining the appropriateness of GAC as a treatment technique. The following section discusses breakthrough in detail.

Breakthrough

Breakthrough occurs when the adsorptive capacity of the carbon for a particular compound is exhausted and that compound begins to appear in the effluent. Because each compound has a unique adsorptive capacity and because influent concentrations vary, compounds will break through at different rates.

The relative order of breakthrough of a group of compounds can usually be predicted based on the mean capacity of those compounds (X/M from isotherm studies). This is true in cases where the compounds have similar concentrations in the influent. Compounds with low capacities will be the first to appear in the effluent, whereas compounds with high capacities would likely appear later. Of the major components of gasoline, the order of breakthrough (from earliest to latest) is generally benzene, ethylbenzene, toluene, xylene, naphthalene, and phenol (Figure 39). Other compounds sometimes found as additives to leaded gasoline—such as methyl-tertiary butyl ether (MTBE), 1,2-dichloroethane (EDC), and ethylene dibromide

MEAN ADSORPTION CAPACITY, mg/gm
@ EQUILIBRIUM CONCENTRATION = 500 mcg/L*

*SOME EXPERIMENTS CONDUCTED AT 1000 mcg/L

Figure 39. Mean absorption capacities of various compounds in gasoline.

(EDB)—might appear in the effluent even before benzene due to their very low adsorption capacities. Table 17 gives the adsorptive capacities for several compounds including gasoline constituents.

In theory, breakthrough occurs when the leading edge of the MTZ just reaches the end of the carbon bed and the effluent begins to contain a detectable amount of contamination (Figure 35). In practice, however, breakthrough usually refers to a point at which the effluent reaches a certain level, or threshold, of contamination. This level is sometimes arbitrarily set, such as the commonly used 5 percent of the influent concentration (Reynolds, 1982); or the level may be based upon environmental regulations, such as discharge limits or drinking water standards. In either case, the level of contamination may refer to the total of all volatiles in the water (TOC is the usual indicator) or to a specific compound or compounds upon which the discharge limits are based.

For example, for an influent stream contaminated by a variety of compounds that is to be used as a drinking water source, an effluent limit may be set for total VOCs. This was the case reported by Mac-Leod and Allan (1983). GAC was used to treat municipal well water contaminated by several organics to levels of 150 ppb. In that municipality, an effluent standard of 5 ppb TOC was established for water for household use. Sometimes an effluent standard is based on a single contaminant. In these cases, the single contaminant may be the com-

pound in the influent stream that is the first to break through, or it may be the compound considered most hazardous.

Usually, the compound with the earliest breakthrough is used as an indicator for carbon change, especially where the effluent is to be used for drinking water. In the case of gasoline contamination, benzene is normally the first compound to break through. For this reason and the fact that benzene is usually considered one of the most toxic components in gasoline, the effluent is typically monitored for benzene, and the carbon is changed when the benzene reaches the threshold concentration. It should be noted that other compounds which may not be found in all gasoline (such as MTBE and EDC) may break through earlier than benzene.

Cost of GAC Treatment

The cost of GAC treatment is dependent on site-specific conditions, and thus varies widely. In general, though, GAC is more expensive than air stripping for similar situations because the capital cost of equipment and the O&M costs for GAC are higher than those for air stripping.
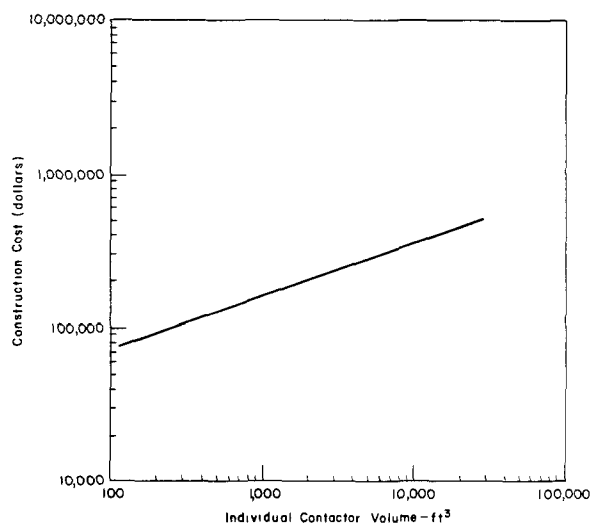
Capital Costs

The capital costs of GAC treatment include the initial carbon charge, carbon vessel, the pumps and piping, electrical equipment, a clearwell (if necessary), housing (if necessary), and engineering design and contingencies. The need for pretreatment may also significantly increase the cost of GAC treatment. The flow rate and the discharge requirements are the criteria used for design and thus have a controlling effect on capital costs. For waters which require removal to nondetectable levels, two carbon contactors normally are operated in series, which will increase the capital cost. Very high flow rates may be treated by using several pressure contactors in parallel or by using a gravity carbon contactor. Gravity contractors are often made of cement, and operate similarly to sand filtration tanks. They can accommodate surface loadings of only 2 to 4 gal/min per ft^2 (Neulight, 1987) and thus must be larger than a corresponding pressure tank, which can treat 5 to 7 gal/min per ft^2. Housing for the contactor(s) is often unnecessary. Engineering and contingencies average about 30 percent of the total capital cost. Figures from Camp Dresser & McKeel (Figures 40 to 43) give approximate construction costs for four types of GAC contactors.
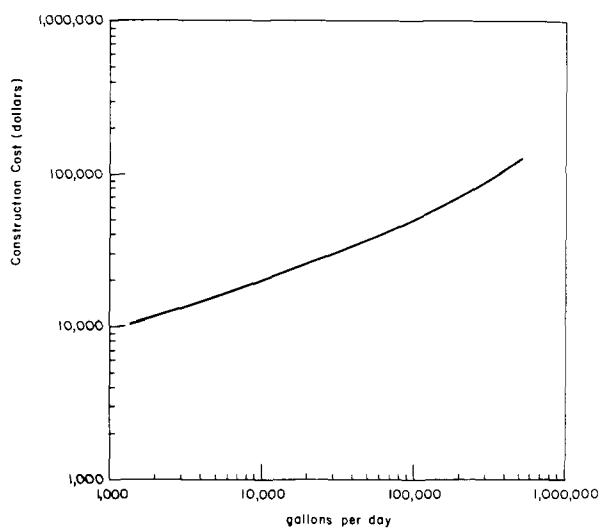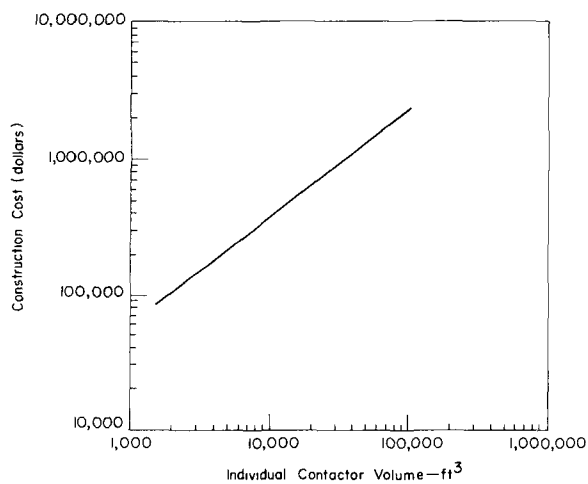
Figure 40. Capital costs of low capacity package GAC contactor.

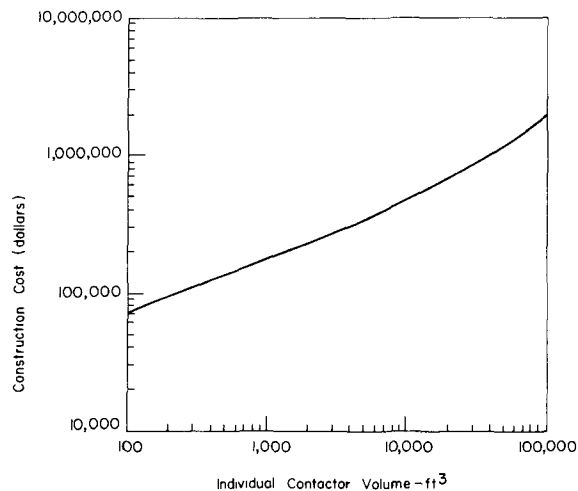Figure 41. Capital costs of pressure GAC contactor.

Figure 42. Capital costs of gravity steel GAC contactor.

Figure 43. Capital costs of gravity concrete GAC contactor.

Operation and Maintenance

The O&M costs include labor, building upkeep, energy costs for pumps and instrumentation, carbon replacement/regeneration, and miscellaneous expenses. Labor, building upkeep, and miscellaneous costs would be similar to those associated with an air stripping facility. Where pressure filters are used, significant savings may occur because the water does not have to be repumped to the system. The cost of the carbon replacement or regeneration can be considerable, in most cases dominating the O&M costs.

Carbon costs depend on the type of carbon used and the carbon usage rate. Carbon prices supplied by a manufacturer (Calgon) ranged from roughly $0.75/lb for their highest quality virgin carbon to $0.60/lb for service carbon (regenerated). The carbon usage rate is often expressed as pounds per thousand gallons of water treated (lb/1,000 gal). The usage rate is influenced by several factors, including the breakthrough characteristics of the contaminants to be removed, the concentration of contaminants, and the required effluent concentration.

Each compound has a unique adsorption capacity that can be described by its Freundlich isotherm (discussed in Section 5.2.8). The greater the X/M value (the weight of contaminants removed per weight of carbon), the lower the carbon usage rate. Studies have shown that the actual carbon usage rate for a typical influent water with several contaminants lies between the rate predicted by the compound with earliest breakthrough and the rate predicted by adding the usage rates of all the compounds (Hall and Mumford, 1987). When designing a carbon system from theoretical isotherms, a large safety factor is normally used. Table 17 and Figure 39 give tabular and graphical representations for adsorption capacities of gasoline components. If the spill contains MTBE, EDC, or EDB, which are sometimes found as additives to leaded gasoline, the carbon usage rate may be even higher. The concentration of the contaminants in the influent stream has a direct effect on the carbon usage rate, as does the background level of organic carbon. Naturally occurring organic carbon includes compounds such as humic substances. The carbon usage rate increases dramatically with increasing levels of contamination in the influent. O'Brien and Fisher (1983) discuss 31 cases of contamination by various compounds where the carbon usage rate ranged from 0.1 to 13.3 lb/1,000 gal. The high figures are associated with very high influent concentrations. A typical leaking UST contamination site has influent concentrations in the range of 100 to 20,000 ppb of TOC.

This wide range accounts for both the size of the

spill and the amount of dilution the gasoline has undergone in the aquifer. Amy et al. (1987) showed that high TOC levels may significantly increase the carbon usage rate. After cleanup has progressed for 6 to 12 months, the influent concentration often drops by an order of magnitude (Bourdeau, 1987) because the source has been removed and the treatment has removed much of the contaminant.

The discharge requirements for the effluent water also influence the cost. Water for potable use will have more stringent treatment requirements than water for groundwater recharge or surface discharge. These requirements may necessitate multistage treatment or a longer contact time, both of which tend to increase overall costs. Multistage operation actually decreases the carbon usage rate, though, because the complete adsorption capacity of the carbon is utilized.

Because so many factors influence the cost of GAC, generalizations are difficult. As mentioned previously, costs differ widely depending on influent concentration, and reported figures are often segregated based on this variable. O'Brien and Fisher (1983) report treatment costs on a per-volume basis. For influent concentrations above 1 mg/L, costs ranged from $0.45/1,000 gal to $2.52/1,000 gal. Costs for lower concentrations (< 1 mg/L) were between $0.22 and $0.54/1,000 gal.

Total capital costs may vary from $100,000 to $800,000 but normally fall in about the $350,000 range. O&M costs range from $25,000 to $250,000 annually; figures of $25,000 to $40,000 are typical. Figures 40 to 43 may be used to find capital costs based on contactor size. Table 16 gives GAC costs relative to air stripping costs.

It should be noted that the relative cost factors in Table 16 are general rules of thumb, and may not be accurate in specific instances. For example, it may be less expensive to use air stripping and vapor-phase GAC than liquid-phase GAC where volatile concentrations exceed 100 ppb, because carbon usage is less in the vapor-phase than it is in the liquid-phase. If volatile concentrations are less than 100 ppb, it may be less costly to use the liquid-phase GAC than the air stripper in combination with the vapor-phase GAC. Capital costs for one air stripper and vapor-phase GAC contactors will be greater than for liquid-phase GAC contactors only. O&M costs for the liquid phase GAC, however, will be greater. Initial contaminant concentrations and length of the cleanup time ultimately determine which alternative is most cost-effective.

Reliability

Activated carbon has been a proven means for removing dissolved organic compounds for over 15

84

years. During this time, it has been used to treat industrial wastewater, public water supplies, and as one of the main corrective action technologies for contaminated groundwater, including gasoline spills. Although GAC is an excellent technique for most organic chemicals found in gasoline, especially those with low solubilities, it is generally not suitable for highly soluble, highly polar, low-molecular-weight compounds. These compounds either do not adsorb significantly, or they break through very early. Methanol, methylene chloride, and acetone are examples of compounds that are not readily removed.

Desorption is a phenomenon that could render GAC unreliable for certain treatment situations. This phenomenon was discussed in Removal Efficiency, p. 70. Regarding desorption, pilot plant studies should be made on a case-by-case basis.

Ease of Operation

The use of GAC requires a different type of monitoring than air stripping for effective operation. Because effluent quality decreases as time passes, the product water must be monitored regularly to ascertain when breakthrough occurs (unlike air stripping, which does not require constant monitoring). At breakthrough, carbon replacement is necessary. As breakthrough becomes imminent, the system will require higher levels of attention. The replacement of carbon in the system requires an engineer and/or company technician to supervise the operation. Depending on the facility, replacing of the carbon can take from 1 to 12 hours; pressure tanks require significantly shorter periods of time than gravity filters. It is advisable to have an engineer make regular inspections to make sure the facility is operating properly.

Limitations

The potential use of GAC to remove all dissolved gasoline constituents from groundwater may be limited by several factors. These factors include the adsorbability of the various components of gasoline, high iron and manganese content of the water, and disposal of the exhausted carbon.

Not every compound found in gasoline is amenable to adsorption by GAC. The compounds MTBE and disopropyl ether (DIPE) are sometimes found as additives to gasoline. Although they can be removed by GAC, both have very high carbon usage rates (Garrett et al., 1986; McKinnon and Dyksen, 1984). Thus, the cost of removing these compounds by GAC is prohibitive, especially if the influent concentrations are substantial. One community is reported to have found MTBE and DIPE in the drinking water at levels of 23 ppb and 14 ppb, respectively. GAC was used to remove the com-

pounds and 40,000 lb of carbon had to be replaced every 4 weeks at a cost of $32,000 per replacement (McKinnon and Dyksen, 1984). Other compounds normally found in gasoline, such as benzene, toluene, xylene, ethylbenzene, EDB, and EDC, are all removable by GAC, with varying carbon usage rates (all less than MTBE).

Therefore, the presence or absence of highly soluble compounds such as MTBE and DIPE, or other additives, may determine the appropriateness of GAC for a particular gasoline spill. None of these compounds are believed to pose as significant a health concern as BTX in general, or benzene in particular. In addition, these additives are not found in all gasolines, unlike the BTX compounds, which are contained in over 99 percent of all gasolines. MTBE, for example, is found in only 10 percent of the gasoline being manufactured today (Garrett et al., 1986).

Iron and manganese levels in the influent water may also limit the use of GAC at a particular site. If these elements are present at levels above 5 mg/L, they must be removed prior to GAC treatment. If the iron and manganese are not removed, they will precipitate onto the carbon during treatment. If this happens, head losses will increase rapidly, the removal of organics will be hindered, and the carbon filter may eventually clog, making it ineffective. At sites where iron and manganese are present at high levels, treatment to remove these elements to acceptable levels must precede use of the GAC unit. This could increase costs substantially or could be impractical due to space constraints.

A major potential limitation of GAC use is the disposal of the spent carbon. Usually, it is either landfilled or regenerated. Regeneration is generally accomplished by heating the carbon to very high temperatures in a kiln to desorb the attached organics and then incinerating the contaminants to destroy them. Regeneration can take place on-site or off-site, but on-site regeneration is economically feasible only for the very largest projects. In general, UST sites would not use this option.

Off-site regeneration facilities have many limitations. After GAC is used to remove contaminants either from the water or in the vapor-phase, it is laden with compounds and could be hazardous. For example, some spent carbon vessels may self-ignite; any carbon with a flash point below 200°F is considered hazardous and may not be shipped over U.S. highways nor accepted by a regeneration facility. Likewise, most facilities will not accept carbon that has been used to remove dioxin or polychlorinated biphenyls (PCBs) because of possible harmful air emissions. In addition, regeneration facilities have air effluent limitations and may not accept all carbon for regeneration. Under

RCRA rules, many contaminant-laden carbons are considered hazardous materials necessitating disposal in a permitted landfill. For example, this is the case for carbon used to remove tetraethyl lead (TEL), an additive in leaded gasoline. Because TEL precipitates onto the carbon, carbon contactor and piping, the carbon and all equipment must be landfilled as a hazardous waste. Another limitation of regeneration facilities is that quantities of carbon of less than 20,000 lb are normally not accepted.

Summary

GAC is an excellent technique to remove organic compounds dissolved in water. Normally, gasoline constituents, particularly benzene, toluene, and xylene, can be removed by GAC to nondetectable limits. But this method is often more costly than air stripping and may not always be the most cost-effective and appropriate method to clean up a gasoline spill. GAC use is limited by site-specific conditions (such as high iron and manganese levels) or by the disposal of the spent carbon.

Using Air Stripping and Granular Activated Carbon in Combination

Background

Discussion in the previous sections has established that air stripping and activated carbon absorption are cost-effective techniques for removing organic chemicals. In most situations involving gasoline-contaminated groundwater, either air stripping or GAC is the technique of choice. However, in some situations, the combined use of air stripping and GAC is the best alternative.

The decision to use the methods in combination would normally be based on effluent quality and financial considerations. In all cases, using both should produce an effluent of as good or better quality than either method alone. A phased approach is typically best suited for leaking USTs. The first phase consists of installing a packed air tower. Its performance can then be monitored to determine effluent concentrations and the need for additional treatment with GAC.

Removal Efficiencies

Where effluent quality is required to be very high, such as potable water situations, the combination of air stripping and GAC is perhaps the best technique to reduce effluent to nondetectable contaminant levels. In these cases, air stripping is used first to remove a large percentage of the VOCs, followed by GAC to remove residual organic contaminants and any nonvolatile compounds to non-

detectable levels. As seen in Figure 44, the use of air stripping as a pretreatment effectively puts an upper bound on the effluent concentrations of VOCs (even at breakthrough) that is considerably lower than if air stripping were not used. Also, as the figure illustrates, GAC life is greatly extended. A properly designed air stripping tower can remove more than 95 percent of the volatile compounds from the influent. More importantly, many of the compounds that are easily removed by stripping, such as benzene, methylene chloride, and dimethylamine, are those with the lowest carbon adsorption capacities. By removing these compounds, the GAC will perform better and last longer, and effluent quality will be improved.
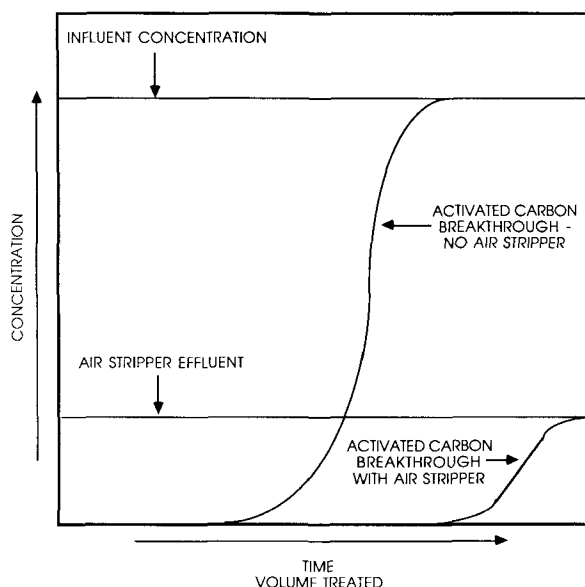

Figure 44. Effect of air stripping as a pretreatment of GAC.

McIntyre et al. (1986), MacLeod and Allan (1983), and Camp Dresser & McKee (1986) have all reported the use of groundwater treatment systems which used air stripping as a pretreatment to GAC treatment. The influent to all the systems studied contained numerous compounds at varying levels, and effluent concentrations were below the detection limits in all cases for all the contaminants.

Cost-Effectiveness

Often, the cost of combining GAC and air stripping is the variable that controls the decision. Because this combination will nearly always yield higher quality effluent than either treatment method alone, it is safe to presume that the combination would be used for any situation where a more cost-effective cleanup would result. Capital and O&M costs on a present-worth basis should be determined for situations in which contaminant removal by a combination of air stripping and GAC might be suitable.

Admittedly, capital costs will increase if both air stripping and GAC are used. The cost advantage of using both methods results from the decreased O&M costs, specifically the lower costs for carbon usage. Adding a stripping tower for use prior to a GAC contactor is justified economically only if the savings on carbon replacement or regeneration equal or exceed the additional capital and O&M costs of the stripper. Stated simply, if the total overall (capital and O&M) cost of treatment is lowered by adding a stripping tower, then that step should always be taken.

Conceptually, this is obvious. For an actual situation, determinations must be made of the decrease in carbon usage due to the air stripper and the associated cost savings. The decrease in carbon usage can be estimated based on the percent removal capability of the air stripping tower. A pilot test, either laboratory or field scale, using water from the site, should normally be performed.

An example of how a combination of the two technologies saves money is given by O'Brien and Stenzel (1984), using TCE. Air stripping was assumed to have removed 80 percent of the influent concentration from (1,000 ppb to 200 ppb). This lowered the adsorption capacity of the carbon from 57 mg/g to 27 mg/g, so the carbon usage rate fell from 0.146 lb/1,000 gal to 0.062 lb/1,000 gal. Thus, an 80 percent decrease in TCE concentration via air stripping resulted in a 57.5 percent reduction in carbon use. Because of chemical similarities between TCE and BTX, comparable reductions could be expected for BTX.

Summary

Using air stripping in combination with GAC is an excellent way to remove high levels of many compounds. The use of air stripping and GAC may be justified in some cases as the least costly alternative. Such cases are likely to be those in which the carbon replacement costs are a significant portion of the overall cost of operation. Usually, these cases will have influent concentrations that are very high and/or increasing, or a contaminant in the influent that breaks through very early.

Biorestoration

Indigenous microorganisms that have been selectively adapted or genetically altered can be used to degrade gasoline components dissolved in groundwater. This use of microbes to renovate contaminated aquifers is termed biorestoration. Although not yet as well known or as widely used as air stripping or carbon adsorption, biorestoration shows promise. Unlike air stripping and GAC, which are separation techniques, biorestoration is a destruction technique. The end products of aerobic microbial degradation are carbon dioxide and water. Also, where applicable, biorestoration is often the cheapest alternative available. Disadvantages of biorestoration include that it cannot be used where a quick startup is needed (biorestoration typically takes 4 to 6 weeks for acclimation), and that it is not successful in a start/stop mode; that is, it must be continued 24 hours per day, 7 days a week.

Biorestoration can be accomplished in situ by either natural or induced methods. Natural in situ biorestoration occurs in aquifers as the microbial populations become acclimated to the pollutant and degrade the contaminants into simpler compounds and ultimately carbon dioxide and water. Induced biorestoration makes use of systems to modify the groundwater regime to optimize degradation rates. Modification of the groundwater environment may be accomplished by various withdrawal, injection, and recirculation pumping systems that mix the contaminant with the groundwater and its microbial population; introduction of elements required for microbial growth including oxygen, nitrogen, and phosphorus, as well as growth substrates; or modification of the chemical characteristics of the groundwater to maximize rates of microbial degradation. Biorestoration can also be accomplished by bioreactors constructed specifically to promote microbial growth in a vessel through which groundwater is pumped.

Regardless of which type of mechanical system is used for biorestoration, the fundamental processes are essentially identical. This section provides a brief overview of the dynamics associated with microbial degradation of gasoline components and a review of the effectiveness, limitations, and costs associated with available biorestoration systems.

Microbial Processes

Microbial degradation of gasoline components can occur by aerobic respiration, anaerobic respiration, or fermentation. Aerobic microorganisms use oxygen in the process of decomposing hydrocarbons; anaerobes use inorganic compounds such as sulfate, nitrate, or carbon dioxide as terminal electron acceptors; and under fermenting conditions, microbes use organic compounds for both the electron donor and acceptor.

Major gasoline components such as the aromatics and alkanes as well as some minor constituents such as EDB and EDC, have been shown to be more readily degradable under aerobic than either anaerobic or fermenting conditions. Also, the by-products of anaerobic decomposition, such as methane and sulfide, and of fermentation reactions, such as organic acids and alcohols, may pose greater system management problems than those associated with the aerobic decomposition products carbon dioxide and water.

Although complete degradation of hydrocarbons will yield carbon dioxide and water, under certain environmental conditions complete degradation

Case Studies

Two examples of actual cases where air stripping and GAC were used in combination are given below. They illustrate typical situations, where air stripping was added after carbon regeneration costs became prohibitive.

Rockaway Township, New Jersey

In 1979, trichloroethylene (TCE) was detected in the municipal wells of Rockaway Township, a small town in north-central New Jersey (McKinnon and Dyksen, 1984). Subsequently, disopropyl ether (DIPE) and methyl-tertiary butyl ether (MTBE) were also found in the water. The source of all three compounds was thought to be a leaking underground storage tank containing gasoline. Concentrations of TCE, DIPE, and MTBE in the water were 200 to 300 μg/L, 70 to 100 μg/L, and 25 to 40 μg/L, respectively.A decision was made to use GAC for water treatment. Based on initial estimates, the carbon supply (two 20,000-lb contactors) was expected to last 6 to 8 months before replacement. However, after just 3 months of operation at a flow rate of 2 million gallons per day, DIPE and MTBE had broken through and were measured in the effluent at levels of 14 μg/L and 23 μg/L, respectively.

The carbon was replaced at a cost of $32,000. Thereafter, carbon was replaced every 2 months. By the end of 1981, the carbon was being replaced every 4 to 6 weeks (the annual O&M cost had risen to about $200,000). Therefore, the decision was made to add an air stripper prior to the GAC, at a capital cost of $375,000.

The stripper was sized to remove 99.9 percent of the influent DIPE concentrations, the least volatile compound (CDM, 1986). After the stripper became operational, the effluent was below detectable limits for all three chemicals. The GAC contactors were subsequently taken off-line, because they were thought to be unnecessary. However, resi-

dents began to complain of a scaling problem in their hot water heaters (the water in Rockaway Township is very hard). It was thought that this problem was caused by the change in the water chemistry during stripping. The GAC contactors were put back on-line, and the scaling problem was solved. The carbon has not had to be replaced since installation of the airstripper.

Acton, Massachusetts

In December of 1978, two of the municipal wells in Acton, Massachusetts, were taken out of service because of the presence of several organic chemicals, including trichloroethylene, benzene, and methylene chloride (MacLeod and Allen, 1983).

GAC was chosen to reduce the contamination from an average influent concentration of 42 μg/L to less than 5 μg/L total, and less than 1 μg/L for any single compound (Nyer, 1984). The high cost of carbon replacement soon became prohibitive. Every 5 months, a complete replacement of 40,000 lb of GAC was required, at a cost of $37,000. In addition, the influent concentrations were expected to rise, causing even more frequent carbon changes. Therefore, the decision was made to use air stripping as a pretreatment.

The column was sized to handle 1 million gallons per day at 95 percent removal of the VOCs. In practice, the removal ranged between 96 and 99 percent (to less than 1 μg/L each), due to the safety factor designed into the system. The stripper cost $31,000; and the building, electrical equipment, and miscellaneous equipment cost $109,000. Over the life of the project, this cost will be more than recovered by the decrease in carbon usage.

may not result. In such instances, intermediary degradation products may accumulate that could either be resistant to further degradation or inhibit further growth (Horvath, 1972). Growth factors which affect the rate of microbial degradation include oxygen requirements, temperature, nutrient availability, and characteristics of the contaminant.

Oxygen Requirements

Aerobic degradation is the most attractive of the microbial processes for breaking down gasoline components in groundwaters because it proceeds at a more rapid rate and does not produce the noxious by-products associated with anaerobic decomposition. In order for aerobic degradation to occur, however, significant quantities of oxygen must be available to the microbes. Barker et al. (1986) calculated that 23.2 mg/L of oxygen are required for degradation of 1 mg/L of benzene, toluene, and xylene in groundwater, and Wilson et al. (1986) noted that in a well oxygenated groundwater containing 4 mg/L of molecular oxygen, microbes can degrade only 2 mg/L of benzene. The solubility of benzene in water (1,780 mg/L) is therefore much greater than the capacity of microbes to degrade the compound under natural conditions. Because microbes will consume oxygen as the hydrocarbon is degraded, an aerobic groundwater can quickly became anaerobic. This onset of anaerobic conditions is the most significant factor limiting the rate of biodegradation in the groundwater environment, according to Raymond (1987).

Because of the importance of available oxygen in microbial degradation, this factor would be most closely controlled when operating an in situ biodegradation cleanup. Three means of increasing the dissolved oxygen content of the groundwater are the injection of air, liquid oxygen, and hydrogen peroxide. According to Raymond (1987), the saturation concentration of oxygen in water from air injection is about 10 mg/L. Hydrogen peroxide injection can provide between 250 to 400 mg/L of dissolved oxygen. The very high amount of oxygen supplied by hydrogen peroxide makes it an excellent choice to maintain the aerobic condition of a groundwater system.

Temperature

Optimal growth of microbial populations responsible for biodegradation of petroleum products occurs between 20°C and 35°C. Microbial degradation rates would be expected to moderate with changes in the groundwater temperatures. Decreasing rates would be expected during winter months in northern portions of the country. Experience has shown, however, that biodegradation can occur at any groundwater temperature once the microbes become acclimated.

Nutrient Availability

Macronutrients, such as nitrogen and phosphorus, must be available for microorganisms in order for biological processes to take place. The quantities of nutrients required for degradation are generally expressed as a ratio of the nutrients to the carbon source. For petroleum products the ideal carbon-nitrogen-phosphorus ratio is 160:1:0.08 (Bartha and Bossert, 1984).

Micronutrients, such as magnesium and sulfur, are also required for optimal growth, although in very small quantities. The micronutrients would not be expected to limit growth of microbes in aquifer systems as often as oxygen deficiency. The specific nutrient requirements needed to optimize microbial degradation of gasoline components is a site-specific factor that must be determined experimentally for each groundwater contaminant problem, considering the relationship of the particular substrate characteristics to the microbial populations.

Characteristics of the Contaminant

The behavior of a mixed microbial population in reaction to the introduction of hydrocarbons will vary depending on the constituents and concentrations of the contaminant.

It has been demonstrated that bacteria, yeasts, fungi, or algae have the capacity to grow on straight-chain and branched alkanes (Sunger and Finnerty, 1984), cyclic alkanes (Perry, 1984), and aromatic hydrocarbons (Ceringha, 1984). Tabak et al. (1981) undertook investigations to determine the biodegradability of various organic contaminants utilizing static culture enrichment techniques and wastewater microbiota. Table 18 summarizes the results of these 7-day screening tests at contaminant concentration levels of 5 and 10 mg/L for selected compounds.

Table 18
Microbial Degradation
Screening Test Results[1]

Compound	Performance[2]	
	5 mg/1	10 mg/1
Benzene	D	D
Ethylbenzene	D	A
Toluene	D	D
Phenol	D	D
Naphthalene	D	D
1, 2-dichloroethane	B	B

[1] Source. Tabek et al., 1981.

[2] Performance at noted concentrations.

A = Significant degradation with gradual adaption

B = Slow to moderate biodegradation concomitant with significant rate of volatilization.

D = Significant degradation/rapid adaption

EPA is currently undertaking a comprehensive research program aimed at determining the land treatability of hazardous wastes (Matthews, 1987). The biodegradation of benzene, toluene, xylene, phenol, tetraethyl lead, EDB, and EDC is being investigated. Interim reports on this work (available in early 1988) should provide significant data for evaluating the fate of gasoline components in soil and groundwater.

Component Concentration

Alexander (1985) reports that the rates of mineralization of some organic compounds are directly proportional to their concentration, and that there is a threshold level below which certain compounds which usually are subject to biodegradation are not converted to carbon dioxide and water. At the higher concentrations of hydrocarbons in groundwater, such as that directly beneath a floating oil slick, microbial toxicity may occur (Cooney, 1984). As the concentration of contaminants decreases and microbial populations become adapted to the compounds, the microbes may be able to overcome the effects of toxicity and degrade the compounds. The resilience of microbial populations to service and repopulate areas in which toxic levels of contaminants were initially present has been demonstrated repeatedly. Therefore, it is anticipated that biorestoration techniques could be adapted to deal with initially high contaminant levels. The more difficult question to address is the level to which a contaminated aquifer can be cleaned up with these techniques.

Litchfield and Clark (1973) found that microbial populations encountered where hydrocarbon contamination exceeded 10 ppm were greater than 10^6/mL groundwater, whereas populations of less than 10^3/mL were encountered where contaminant levels were less than 10 ppm. As Cooney (1984) reports, the rate of microbial degradation may be slow or nil below a certain threshold level. At low substrate concentrations, other mechanisms may be more significant in reducing contaminant levels.

Schmidt and Alexander (1985) report on the effects of low levels of organic carbon on the degradation of low concentrations of substrate. They demonstrated that the rate and extent of biodegradation of low concentrations of synthetic organic compounds may be controlled by the presence of other organic molecules in the system. Pure cultures of bacteria were demonstrated to utilize low levels of aromatics simultaneously in the presence of other organic compounds. Theoretically, the addition of organic substrates in biorestoration systems could further enhance biodegradation of hydrocarbons in groundwater at low levels.

Degradation of compounds may also occur in situations wherein the microbe effecting degradation does not derive any nutrients or energy from the process. This process, co-metabolism, is defined by Horvath (1972) as any oxidation of substances that takes place without the energy derived to support microbial growth. Co-metabolism may be a significant process for degradation of low levels of hydrocarbon contaminants in groundwater. This process should be evaluated on a site-specific basis when biorestoration techniques are being considered since gasoline components such as xylene and ethylbenzene have been demonstrated to be subject to co-metabolism (Horvath, 1972).

Bouwer and McCarty (1984) showed that trace levels of the aromatic hydrocarbons ethylbenzene, styrene, and naphthalene could be reduced significantly in the presence of a primary substrate. Specifically, with acetate as a primary substrate at concentrations of 1.0 mg/L, ethylbenzene levels were reduced from 9.1 µg/L to 0.1 µg/L. Ethylbenzene present alone at these low concentrations could not trigger biodegradation, whereas the presence of acetate as a primary substrate was effective in stimulating it.

Effectiveness

The effectiveness of biorestoration in laboratory studies has been demonstrated to be significant. However, actual field applications of biorestoration techniques underscore their site specificity and variable nature.

Amdurer et al. (1986) summarize case histories of in situ treatment techniques applied to subsurface contaminants. Among the case histories summarized is the Biocraft site in Waldich, New Jersey. At this facility an estimated 30,000 gal of methylene chloride, acetone, n-butyl alcohol, and dimethylaniline leaked from USTs to subsurface soils and groundwater. The biorestoration system constructed for use at this site was comprised of a downgradient dewatering trench and well, two mobile biological activating tanks, two mobile settling tanks, and two upgradient reinjection trenches (Figure 45). The system was used to treat 14,000 to 20,000 gal of groundwater per day. The median reduction of contaminant mass ranged from 88 to 98 percent, except for dimethylaniline for which only 64 percent of the mass was reduced. Each pass through the system had a retention time of 12 hours. Operation began in 1981, and as of 1985, 95 percent of the contaminants in the groundwater had been removed.

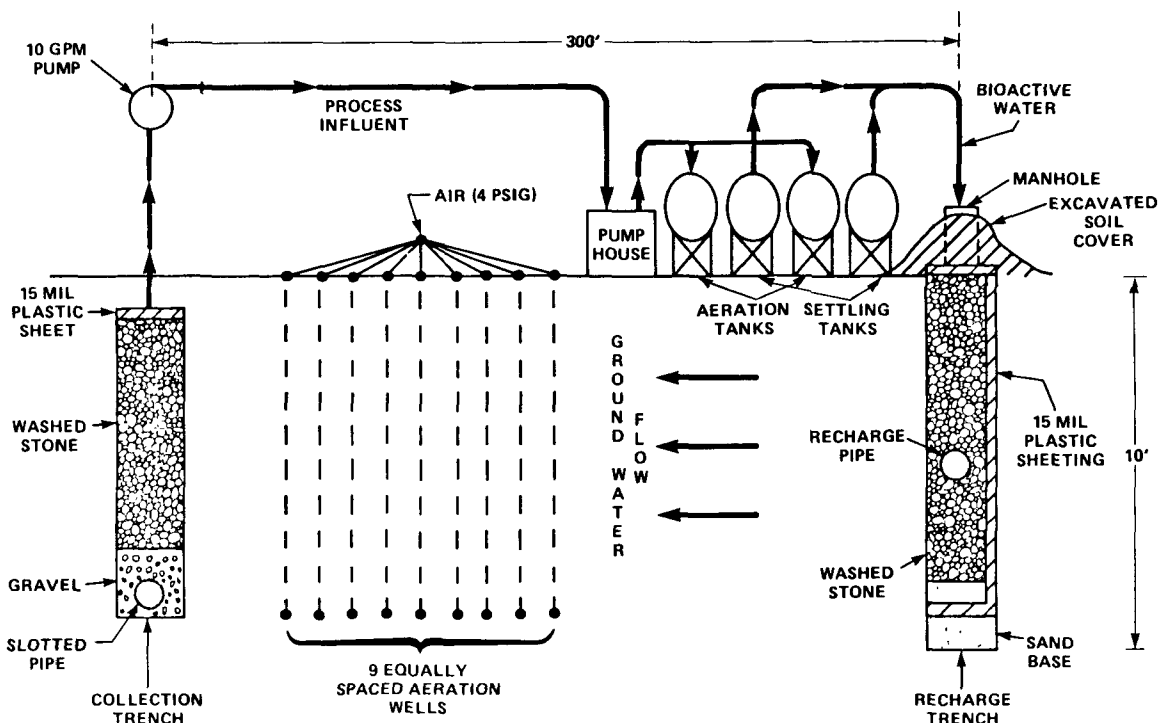Yaniga (1982) reports on the biorestoration of a groundwater aquifer in Montgomery County,

Figure 45. Flow diagram of biocraft biorestoration.

Pennsylvania, where gasoline had leaked from an UST at a service station. The contaminant plume initially contained up to 15 ppm of dissolved hydrocarbons. The biorestoration system for this site consisted of a central pumping well and a reinjection gallery situated over the pit where the tank had been. The extracted groundwater was passed through an air stripping tower to remove VOCs then oxygenated and enriched with nutrients before being reinjected. After 20 months of system operation the hydrocarbon concentration in the groundwater aquifer was reduced to 2.5 ppm.

Yaniga and Smith (1985 and 1986) report additional information on the above site following 3 years of the abatement program. They indicate that from 30 to 3,500 gal of oxygenated and nutrient-rich water per day was injected into the infiltration gallery, and after the first 11 months of operation, the organic content of the groundwater was reduced by 50 to 85 percent. The authors report that use of hydrogen peroxide is superior to use of air in oxygenating the groundwaters. Although others have reported that hydrogen peroxide can cause microbial toxicity, Yaniga and Smith (1986) indicate that at a 100-ppm concentration it did not kill, but rather enhanced, microbial growth and yielded a concentration of 50 ppm of oxygen in the groundwater.

Barker et al. (1987) undertook investigations to evaluate the fate of benzene, toluene and xylene (BTX) in a shallow sand aquifer by intensively monitoring the aquifer following the injection of 1,800 L of water containing about 7.6 mg/L of BTX. The attenuation of these components was evaluated. The field studies were compared to microcosm studies in which conditions approximating that encountered in the field were maintained.

The study conclusions support the general findings that oxygen is rate-limiting with regard to microbial degradation of petroleum products in the groundwater regime. BTX components were found to persist in aquifer layers where dissolved oxygen levels were near zero. In a little over 1 year of injection of the BTX, complete natural removal was observed in the field experiment, with benzene exhibiting the greatest resistance to breakdown.Chan and Ford (1986) report on the use of both in situ and bioreactor systems to remediate a 22,000-ft^2 site contaminated with No. 2 diesel fuel. The estimated removal efficiency of the combined system following 100 days of operation was 80 percent. The bioreactor was 16 times more efficient than the in situ process in removing contaminants from the groundwater. The increased efficiency was attributed to the higher oxygen concentrations which could be maintained in the bioreactor (9 mg/L) as compared to the in situ levels (2.5 mg/L).

Dorr Oliver Incorporated has developed two bioreactor systems, OXITRON[R] and MARS[TM], that potentially could be utilized for the biorestoration of groundwater contaminated with gasoline. The OXITRON[R] system is an aerobic or anoxic fluidized bed system that uses either sand, activated carbon, or other media on which biomass buildup occurs (Figure 46). Contaminated groundwater is passed through the system from the bottom of the reactor vessel at sufficient velocity to fluidize the bed. Because of the increased space between fluidized particles, as compared to suspended growth media systems, 5 to 10 times greater biomass concentration is reportedly achieved. The increased biomass concentration reduces the hydraulic retention time required for treatment.

MARS[TM] (stands for membrane aerobic or anaerobic reactor system) uses a well-mixed suspended growth reactor and ultrafiltration system (Figure 47) for biorestoration of groundwater (Sutton, 1986).
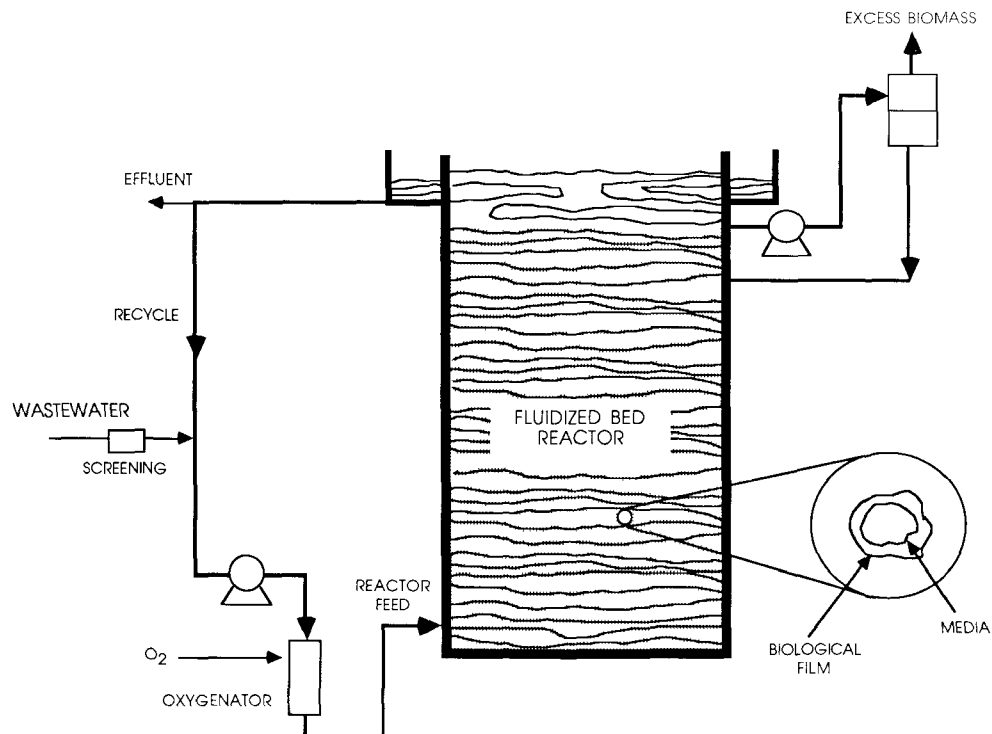

Figure 46. Schematic of Oxitron® process.

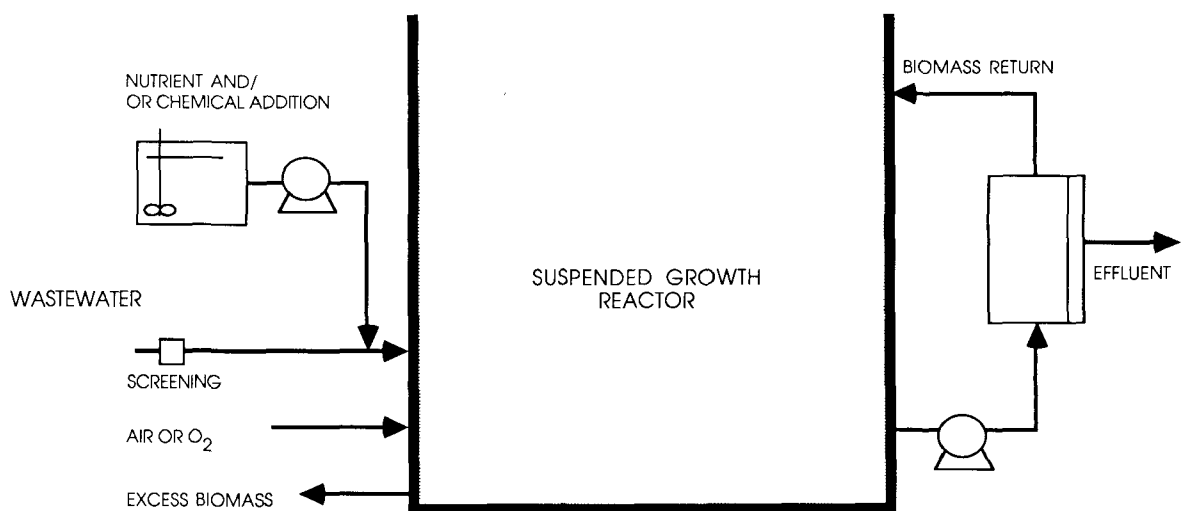Figure 47. Schematic of Mars™ process.

Site-specific evaluations of the degradability of the groundwater constituents in either system are needed, as with all bioreactor or in situ techniques, but Dorr Oliver has used these systems successfully for treating various wastes similar to those found in gasoline-contaminated groundwaters, including benzene and toluene.

Although indigenous microbial populations have the capability of degrading hydrocarbons, interest in using mutant, genetically engineered or laboratory-adapted organisms has increased in recent years.

Polybac Corporation, located in Allentown, Pennsylvania, markets Polybac and Hydrobac, formulations described as mutant, adapted microbes and biochemical accelerators. Polybac is made specifically for municipal and food processing wastewater treatment systems, and Hydrobac is for petroleum refinery/petrochemical plant wastewaters. Other products available from Polybac Corporation. include Petrobac for degrading hydrocarbons in salt water and Phenobac for degrading hydrocarbons in fresh water. Polybac Corporation also markets bioreactor systems and services (CTX-BIOX System) with reported removal efficiencies "in excess of 99 + % for most organic compounds" (Polybac, 1980; 1981).

Solmar Corporation of Orange, California, markets microbial cultures for use principally in wastewater collection and treatment systems. One product is Advanced BioCulture Formulation L-104, which is used for "heavy, tarry types of oils, coal tars, and organic sludges." It is reportedly well suited for aromatic and phenolic wastes (Solmar, 1984).

Other firms providing groundwater biorestoration services and systems include:

- Groundwater Technology
  Chadds Ford, Pennsylvania

- Groundwater Decontamination Systems, Inc.
  Paramus, New Jersey

- NEPCCO
  Foxboro, Massachusetts

- Detox
  Dayton, Ohio

- Emtek
  Bedford, New Hampshire

- TerraVac, Inc.
  San Juan, Puerto Rico

Limitations

Limitations on the use of biorestoration techniques relate to sociopolitical issues as well as technical factors. Because in situ treatment is accomplished largely underground, little if any evidence of activity may be discernible by the general public. This lack of observable activity could lead to a public perception of no-action. In general, the public may be more prone to respond positively to corrective actions that manifest significant levels of activity, such as air stripping. Therefore, efforts to educate the public about the mode and effectiveness of in situ degradation may be required where high levels of public awareness exist.

The technical limitations of biorestoration techniques may be related more closely to site-specific characteristics than to the overall theoretical ability of microorganisms to degrade gasoline components in groundwater. As discussed, microbial growth factors appear to be readily modified either in situ or by bioreactors to allow for degradation of gasoline in groundwater systems. Degradation of hydrocarbons to ppm levels should be relatively attainable; however, reaching ppb levels may require that the system be manipulated to encourage co-metabolism or degradation in the presence of an added primary substrate. These limitations can be assessed only by performance of site-specific laboratory and pilot-scale evaluations. It is possible to meet the proposed maximum contaminant level of 5 μg/L for benzene and 0.44 mg/L for xylene with a system that is appropriately designed and optimally operated.

The fact that biorestoration can work in saline as well as fresh systems makes it adaptable to situations where other treatment systems may not be suitable.

Biorestoration may pose major limitations in terms of the ability of the recovery system to capture contaminated groundwaters and the restrictions on reinjection of treated or nutrient enriched waters into the aquifer system. Capturing hydrocarbon-contaminated groundwater is an engineering issue that should be readily addressable based upon site-specific hydrologic considerations, whereas reinjection involves institutional issues that may be more difficult to overcome.

Reinjection of treated waters, which in some cases may be nutrient enriched, potentially could be seen as an environmental threat in and of itself. In some situations, there could be a problem obtaining permits necessary for reinjection. Manipulating groundwater characteristics to optimize microbial degradation may require the introduction of various growth substrates and nutrients such as nitrogen. Although these materials should be applied at the rates required for microbial metabolism, excess loadings might be needed to ensure adequate distribution in the aquifer.

Because complete hydraulic isolation may not be possible in most situations where biorestoration is employed, the added materials could move beyond the zone of contamination. These potential impacts must be assessed in relation to the potential benefits derived from biorestoration. In undertaking any biorestoration system, therefore, consideration must be given to the tradeoffs between injecting materials into the groundwater and remediating the gasoline components to acceptable levels.

Costs

Costs for biorestoration are dependent on specific factors such as hydrogeology and groundwater chemistry, groundwater quantity and quality, the quantity of contaminants, and the required level of cleanup.For the first case history discussed in this section, the total capital cost for remediation was $926,000 (Amdurer et al., 1986). Approximately $446,000 was expended during the feasibility evaluation, which was completed within 2 ½ years. The O&M for treating groundwater once the system was operational were $0.0165/gal (about $225.50/d for 13,680 gal/d).

Other representative cost estimates for biorestoration projects are listed below:

* Ehrenfeld and Bass (1984) estimate the 6-mo cost for in situ biodegradation of wastes on a 1-acre site to be $1,200.

* A. M. Kirby of Suntech, Inc. estimates costs of approximately $50,000 for a 5-acre site with a 6-mo clean-up period.

* Richard L. Raymond, Jr., of Biosystems estimates a cost of $4 to $6/lb of contaminant removed (compared to $15 to $20/lb for air stripping and $40/lb for carbon adsorption).

* Dr. Ralph Portier of Louisiana State University estimates a cost of $30 to $50/yd^3 of contaminated soil (compared to $125 to $130/yd^3 for hauling and disposal of the soil).

Summary

Although biorestoration techniques provide methods whereby groundwaters contaminated with gasoline components can be effectively remediated, the technology has not been widely applied. Packed air towers and activated carbon adsorption systems are the preferred technologies for groundwater treatment. Biorestoration does show promise, however, as a cost-effective alternative. Biorestoration accomplished in situ and in bioreactors has been demonstrated to be effective in degrading hydrocarbons, although the degree of cleanup is highly dependent on specific environmental conditions affecting microbial growth. The time required for biorestoration techniques to effec-

tively mitigate gasoline-contaminated aquifers is expected to be on the order of years rather than the shorter times needed for physiochemical techniques such as air stripping or carbon adsorption.

Biorestoration techniques should be considered for gasoline-contaminated aquifers where control of contaminant migration can be achieved hydraulically. Because these corrective action techniques require minimal construction impacts, they are highly suited for implementation at active facilities.

One of the main advantages of biodegradation over other techniques is that the contaminants are completely destroyed, with the end products of aerobic degradation being carbon dioxide and water. Air stripping and activated carbon, on the other hand, are both separation techniques whereby the contaminant is simply transferred to a different medium. Thus, biorestoration avoids problems such as the vapor-phase treatment (associated with air stripping) and the disposal or regeneration of hazardous spent carbon.

The most beneficial aspect of biorestoration techniques may be that they can be used with other physiochemical corrective actions. For example, in situ biorestoration techniques can be coupled with soil gas venting and groundwater extraction and treatment techniques to accelerate restoration of the aquifer. Bioreactors can be used with air strippers or carbon adsorption systems to yield high levels of treatment.

Because of the relatively low costs associated with biorestoration techniques, application of these methods to gasoline contaminated aquifers should be given serious consideration during project development and scoping.

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Section 6

Point-of-Entry Treatment and
Alternate Water Supplies

Gasoline spills and underground storage tank (UST) leaks can contaminate groundwater that supplies private wells. High levels of dissolved gasoline constituents such as benzene, toluene, xylene, ethylbenzene and other volatile organic compounds (VOCs) can render well water unfit for human consumption. Because aquifer restoration frequently takes months or even years to complete, users of well water must find alternative drinking water sources. Two common alternatives include point-of-entry treatment in the homes where contaminated water is found and extension of the existing water distribution system to the well user. In the following section, these two options are analyzed for their cost, feasibility, and limitations.

Point-of-Entry Treatment

Background

The constituents of gasoline most commonly found at spills and at leaking UST sites include the aromatics benzene, toluene, and xylene (BTX). Aromatics can comprise up to 20 percent of the weight of gasoline and even higher percentages of the soluble fraction. Of these three constituents, benzene is of greatest concern; it has been shown to cause cancer in humans. Also, benzene is highly soluble, and it can move easily into groundwater. As a result, a principal design criterion of groundwater treatment systems is the removal of benzene.

The benefit of point-of-entry treatment devices is that they can remove dissolved chemicals from gasoline-contaminated well water at a single point. There are two types of devices used. The term point-of-use applies to devices for individual taps or for drinking water only; point-of-entry devices are used to treat all water as it enters the home or building. Small-scale equipment is available that can treat a single faucet, while larger units installed adjacent to the water pump can treat enough water for an entire household. A significant problem associated with single-tap and drinking-water-only treatment is noted in research done by NUS corporation (Symms, 1986). Symms contends that taking showers in water containing groundwater contaminants probably leads to "far greater exposure to the chemicals than drinking the same water," because gasoline is a mixture of highly volatile hydrocarbons that vaporize readily in the presence of oxygen. By drawing tap water contaminated with gasoline components, the hydrocarbons are allowed to vaporize. Daily exposure to gaseous hydrocarbons for weeks or months can pose a significant health threat. For this reason, point-of-use treatment devices cannot be said to eliminate totally the health risks associated with gasoline-contaminated well water. Hence, the following discussion covers only point-of-entry devices.

Point-of-Entry Devices

Several different processes have been successfully adapted to point-of-entry devices for treating contaminated well water as it enters the home. The most common treatment processes are reverse osmosis, ion exchange, distillation, aeration, and carbon adsorption. Although these processes have been widely applied, they are not all equally appropriate for removing dissolved gasoline constituents.

Reverse Osmosis

Osmosis is the process by which a fluid diffuses through a semipermeable membrane until there is an equal concentration of fluid on either side of the membrane. In reverse osmosis the natural osmotic gradient is reversed, so that the fluid is forced through the membrane, producing unequal concentrations on either side of the membrane. With contaminated well water, high pressure pumps (as high as 200 psi) move the water through the membrane and separate the contaminants. Reverse osmosis is most effective in removing chemicals with a molecular weight greater than 250. Benzene, toluene, and xylene have molecular weights

of 78, 92, and 106, respectively, and are therefore too light to be retarded by the membrane. Another drawback to using reverse osmosis point-of-entry devices is that filtering enough water to meet household needs would require a costly high pressure, commercial system and a large (60-100 gal) storage tank.

Ion Exchange

Ion exchange is generally associated with water softening. The process involves replacing cations such as calcium and magnesium, which cause hardness, with other cations, usually sodium. Because organic compounds are not ionic, ion exchange would not be an effective point-of-entry treatment device for recovering dissolved gasoline constituents from well water.

Distillation

Distillation is the process by which water is vaporized and then recondensed into liquid. During distillation, volatile organics also vaporize, but because they are not easily recondensed, the organics are effectively separated from the water. The main drawbacks to using distillation point-of-entry devices are that vaporization requires much energy and costs are high. Also, in most cases, not enough water can be produced to meet household needs. Since the vaporized organics are generally vented to the atmosphere immediately outside the home, they could continue to pose a health hazard.

Aeration

Aeration is the process by which the surface area of water exposed to oxygen is increased allowing a large fraction of the organic compounds to volatilize. Aeration is capable of 90 to 95 percent removal efficiencies and is most effective in reducing high (> 100 ppb) levels of volatile contaminants (1 ppb = 1 μg/L. Since aeration is less effective at removing low (< 10 ppb) contaminant levels, it is often used as pretreatment for other removal processes. As a point-of-entry treatment, aeration has not been widely used because it must be done in a closed vessel vented to the outside. Also, aeration

is a complicated and expensive process requiring an additional water pump to move water through the aerator.

Carbon Adsorption Systems

Usefulness of Carbon

Several factors make carbon adsorption the most widely used point-of-entry treatment. The prime benefit of using carbon is its ability to adsorb and concentrate organic compounds several thousandfold from dilute solutions. For a discussion of carbon porosity, see Activated Carbon Adsorption in Section 5. Carbon is also generally less expensive and easier to work with than any of the other treatment types. Because of the prevalent use of carbon adsorption in point-of-entry applications, there is a well established network of carbon adsorption equipment manufacturers and service companies.

Designing Carbon Adsorption Point-of-Entry Treatment Systems

Isotherms are critical components in the design of carbon adsorption systems. They are used to describe the capacity of carbon to adsorb dissolved compounds from solution. The calculations for determining carbon's capacity and Freundlich isotherm relationships are discussed in detail in Section 5. Table 19 illustrates a case in which benzene, toluene, and xylene were found in groundwater.

Using the concentrations shown and the K and 1/n values determined experimentally, X/M can be calculated for each chemical. Next, to determine the carbon requirement (the amount of carbon necessary to adsorb the chemical from a liter of solution), the initial concentration of the chemical is divided by X/M. The resulting value, which has the units g/L, is converted to lb/1,000 gal. The sum of the three single-solute carbon requirements is the total carbon requirement. This number can be used to calculate the lifetime of the carbon in the treatment unit.

Table 19
Three Cases of Carbon Usage

Chemical	Concentration (mg/L)	K	1/n	X/M (mg/g)	g/l	Carbon Requirement (1b/1,000 gal)
Benzene	10	4.1	0.545	14.38	0.695	5.860
Toluene	6	26.1	0.44	57.42	0.104	.878
Xylene	8	85	0.19	126.18	0.063	.532
					TOTAL	7.27

In the carbon tank life calculations shown below, a standard 1.5 ft^3 carbon column (a size typically employed in home treatment systems) is used:

Bed Volume: 1.5 ft^3

Bed Mass: 34 lb 23 lb/ft^3

Tank Capacity: (34 lb/tank) (7.27 lb/1,000 gal) = 4,677 gal/tank

Assumptions: 2 people 70 gal/day

Service Time: (4,677 gal/tank) / (140 gal/day) = 33 days/tank

Estimated Tank Life: 1 month/tank

The estimated tank life is the amount of time that the carbon in the tank can remove contaminants before "breakthrough" occurs (tank life calculations assume that concentrations and adsorption rates are static). Once contaminants are found in the tank effluent, breakthrough is said to have occurred and it is necessary to replace the carbon in the tank.[1]

In most point-of-entry applications, two carbon columns of equal volume are used in series to ensure that if breakthrough occurs in the first column, contaminants will be adsorbed by the second. Because the estimation method used above is less accurate when predicting low-level breakthrough, tank life estimates should be conservative.

Also, as the number of compounds in solution increases, the design of carbon adsorption systems becomes more complicated. For these reasons, total carbon requirements are based on the sum of the single-solute carbon requirements, rather than on the one solute that has the highest carbon requirement and can be expected to break through first. Hall and Mumford (1987), however, concluded that in most cases the observed equilibrium capacity of the carbon normally lies between the amount predicted using the single-solute with the greatest carbon requirement and the amount predicted using a simple summation of single-solute requirements.

Carbon Adsorption Efficiency

Case studies and experiments have demonstrated that carbon has the ability to remove a variety of organic solutes in water to very low levels. In 11 chemical spills and 18 groundwater contamination case studies cited by Brunotts et al. (1983), activated carbon was shown to remove most contaminants to within 1 ppb (.001 µg/L). Carbon has also been shown to be effective in removing gasoline constituents from contaminated groundwater. Hall and Mumford (1987) discussed the use of carbon adsorption as a point-of-entry treatment in both a gas station and a private home where gasoline constituents were found in the well water. In each case two carbon tanks in series were used, and more than 99 percent of the dissolved gasoline constituents was removed.

Limitations

The use of carbon adsorption point-of-entry water treatment devices is limited by several factors. As noted earlier, water pH, temperature and hardness, as well as solute type and concentration, all influence the adsorption capacity of carbon. Also, certain types of pathogenic bacteria that frequently colonize on the carbon in treatment units can be released to the treated water. To mitigate these problems and enhance the adsorptive capacity of the activated carbon, it is necessary to analyze the quality of the influent water and then either set up a pilot system to ensure adequate water treatment or closely monitor the full-scale system for contaminant breakthrough or any other undesirable effects. Most water quality complications (e.g., pH, hardness, iron, bacteria, viruses) can be reduced or treated so that the carbon adsorption unit can operate effectively, but the importance of effluent monitoring cannot be overemphasized. Researchers note that effluent monitoring is one of the most critical criteria in designing and implementing point-of-entry carbon adsorption systems (Hall, 1987).

Perhaps the most serious limitation associated with carbon adsorption point-of-entry treatment systems installed in the home is that significant changes in the concentrations of contaminants in the influent water may go undetected by the home-

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[1] The general order of breakthrough—from earliest to latest—of toxic gasoline compounds is benzene, toluene, ethylbenzene, xylene, naphthalene, and phenol. It should be noted that gasoline additives ethylene dibromide (EDB), ethylene dichloride (EDC), MTBE, and DIPE may break through even before benzene, due to their low carbon adsorption capacities.

owner until periodic (monthly or bimonthly) water quality analysis is performed. The design of the carbon adsorption system is based on a set of known or predicted maximum contaminant concentrations. Should these concentrations fluctuate and exceed the design capacity of the system, or if water quality complications reduce the effectiveness of the carbon, earlier breakthrough of contaminants could occur. In such a situation, residents would be unaware that contaminants had moved through the treatment system. As a precaution, water quality analyses could be performed more frequently. However, because each test could cost as much as $250, the additional cost to the homeowner (not to mention the added inconvenience and anxiety) may make other water treatment alternatives more appealing. These sentiments will be especially prevalent in larger communities where many homes are affected.

Costs of Carbon Adsorption Point-of-Entry System

Factors that influence the costs of carbon adsorption point-of-entry treatment systems are:

- Types of contaminants present
- Concentrations of contaminants in the influent
- Water quality complications in the influent
- Flow rates
- Amount of carbon used
- Chemical testing

Tables 20, 21, 22, and 23 show costs typically associated with point-of-entry treatment systems installed in the home. These figures are based on data generated for a 1984 Camp Dresser & McKee project in Rhode Island; a 1986 project by Culligan, Inc., also in Rhode Island; and from a 1987 Hall and Mumford project in Wisconsin.

The total equipment and annual operating costs for carbon adsorption point-of-entry treatment systems are most dependent on the types and concentrations of organic compounds in the influent water. Each organic compound has a characteristic affinity for carbon, which ultimately determines how long the carbon will last before its adsorption capacity is exhausted. Some highly soluble organic compounds found in gasoline, such as MTBE and DIPE, have very high carbon usage rates. If these compounds are found in high concentrations in the influent water, frequent carbon replacement will be required, thus making carbon adsorption considerably more expensive. Likewise, as the concentration and number of organic compounds in solution increases, the life of the carbon decreases, and it must be replaced more often.

Water quality problems such as low pH; high iron, calcium, and magnesium content; the presence of high molecular weight (> 200) organics; and the presence of bacteria and viruses may all reduce the adsorptive capacity of carbon. Water treatment equipment is available which can remove these complications; however, as shown in Table 24, they can add considerable costs to the system.

Changes in the flow rate through the system also have a direct impact on costs. Assuming concentrations are static, higher flow rates caused by increased water use in the home will lead to more rapid carbon exhaustion and more frequent replacement. Thus, as flow rates increase, so do costs.

The cost of high quality, activated, virgin carbon is approximately $1.00 per pound. Enough carbon to fill a 1.5 ft^3 tank (34 lb) would cost roughly $34. The costs shown on Table 20 for carbon replacement and disposal are higher than this because they reflect the associated labor, equipment, and carbon disposal costs. As mentioned previously in Section 5, regenerated carbon is not used in drinking water treatment systems. The rate at which carbon is exhausted—and thus the interval between replacement—is a function of the concentrations and types of organic compounds in the influent water. Chemical testing, on the other hand, can be considered a variable cost. Once the system is in operation and the estimated carbon tank life has been verified, the frequency of effluent testing can be reduced; however, it still must be done periodically as a safeguard against early breakthrough. Hall and Mumford (1987) conclude that it is more cost-effective to replace the carbon at the end of its estimated tank life than it is to continue monthly testing of the effluent for VOCs. In point-of-entry treatment systems where only 30 to 40 lb of carbon is needed per column at any one time, carbon costs may seem insignificant in comparison to costs for larger scale wastewater treatment plant carbon beds, which can require up to 40,000 lb of carbon each. However, when organic compound concentrations in the influent are high and frequent carbon replacement is necessary, the annual carbon budget may become considerable, especially for a homeowner assuming the cost burden.

Feasibility of Carbon Adsorption Point-of-Entry Treatment

Few studies have been done to determine the maximum influent concentrations for which carbon adsorption point-of-entry treatment is feasible. The higher the influent concentrations of organic compounds, the more rapidly the carbon is exhausted and the sooner it will have to be replaced. Likewise,

Table 20
Carbon Adsorption Point-of-Entry Treatment System Costs

Component	Cost[1]
1 - 1½ ft³ Carbon Column	$700-800
Installation & Plumbing	$100-150
Carbon Replacement & Disposal	$100-200/replacement
Chemical Testing (9 VOCs)[2]	$250/test

[1] All costs are based on average annual water usage estimates for 2-3 person household at 80 gpcd (160-240 gallons per household per day).
[2] It is assumed that EPA Method 624 is used to test for the presence of benzene, toluene, xylene and six other VOCs (volatile organic compounds).

Table 21
Cost of Proposed Camp Dresser & McKee Project

Component	Cost[1]
2 Carbon Columns (1 ft³)	$900-1000
Installation & Plumbing	$100-150
Carbon Replacement & Disposal	$200 x 6 per year = $1800
Chemical Testing	$250 x 12 per year = $3000
Total Per Household Per Year =	$5800-5950

[1] Note: These are average costs for 10 homes.

Table 22
Cost of Culligan Project, Inc. in Rhode Island, 1986

Component	Cost[1]
1 Carbon Column (1⅓ ft³)	$725
Installation & Plumbing	$130
Carbon Replacement & Disposal	$190 x 3 per year = $570
Chemical Testing	$250 x 6 per year = $1500
Total Per Household Per Year =	$2925

[1] These are average costs for 13 homes which received point-of-entry carbon adsorption systems. The systems were installed for 2½ years while a centralized water distribution network was being extended to the homes.

Table 23
Cost of Hall and Mumford Project in Wisconsin, 1987

Component	Cost[1]
2 Carbon Columns	$2950[2]
Installation & Plumbing	$100
Carbon Replacement & Disposal	$100 x 4 per year = $400
Chemical Testing	$150 x 12 per year = $1800
Total Per Household Per Year =	$5250

[1] Note: These are average costs for a service station and private home which received point-of-entry carbon adsorption systems.
[2] Cost includes a chemical feed unit, retention tank, and ion exchange softening unit.

Table 24
Water Treatment Equipment Commonly Used in Carbon Adsorption Systems

Equipment	Purpose	Cost[1]
Chemical feeder	Raise pH, precipitate iron	$500 00
Ion exchange softener	Remove Ca and Mg hardness	950.00
Manganese greensand filter	Filter out Fe + 2 and Fe(OH)3	950.00
Calcium carbonate/magnesium oxide bed	Remove iron	825.00
120 Gallon retention tank	Mixing, flocculation, precipitation	525.00
Reverse osmosis	Reduice mineral content, remove high molecular weight organics, bacteria, viruses	730.00

[1]Costs are from Culligan, Inc. Costs are for the unit only and do not include installation or maintenance.

the higher the influent concentrations, the more concern there is that early breakthrough will occur; and, therefore, more effluent testing for VOCs is performed. To further complicate the economic considerations, homeowners may insist that additional safeguards such as point-of-use treatment or bottled water be provided. Also, for well water with water quality parameters that are adverse to carbon adsorption (such as low pH or excessive hardness), additional water treatment units may be necessary, which would add considerable costs to the system. Therefore, the decision to apply point-of-entry treatment should be based on site-specific conditions, including the overall quality of the influent water and the needs of the homeowner. Finally, because the total cost of remediating a gasoline spill depends on the number of homes affected, at some point the marginal cost to the polluter; Federal, state, or municipal financiers; or the homeowners of installing and maintaining point-of-entry treatment systems will exceed the cost of other treatment alternatives.

In considering carbon adsorption and other point-of-entry treatment systems, it should also be recognized that their use in treating gasoline-contaminated well water is a newly applied remedial strategy. Although equipment and service companies are available in most towns and cities, the retailers and service personnel may not fully understand the capabilities and limitations of carbon adsorption units in removing organic compounds.

Furthermore, most research projects and home installations have focused on carbon adsorption (and other point-of-entry treatment systems) as an interim remedial action rather than a long-term solution to the contamination problem. Commonly, most point-of-entry treatment projects of this kind

have lasted 1 to 3 years. The interim is used to implement other remedial action such as aquifer restoration, to locate suitable alternative water supplies such as new well fields, or to extend water distribution mains from local systems.

Extension of Existing Water Distribution System

Alternative Water Supplies

In situations where gasoline from surface spills or leaking USTs threaten domestic well fields, extending nearby water distribution systems is often an appropriate long-term solution to the problem of supplying the affected homes with clean water. Supplying homes with bottled water or installing point-of-use and point-of-entry treatment systems are considered interim remedies only, whereas extending the local water distribution system is a permanent solution and is often more acceptable to homeowners. Other long-term solutions such as drilling new wells in as yet uncontaminated parts of the well field may be impractical, especially if the new wells are located downgradient of the spill site where they could eventually be contaminated by the migrating gasoline plume.

Costs of Extending Distribution Systems

Cost is one of the primary considerations in extending existing water distribution systems to homes with contaminated well water. Table 25 lists costs typically associated with installing water transmission and distribution mains. A "transmission" main transports water over long distances from centralized pump stations to "distribution" mains; distri-

Table 25
Cost Breakdown Per Linear Foot for Water
Distribution and Transmission Mains

Cost Category	6-inch		8-inch		12-inch	
	Dist	Trans.	Dist.	Trans.	Dist.	Trans.
Excavation	$ 8.70	$ 8.70	$ 8 70	$ 8.70	$ 9.00	$ 9.00
Pipe	6.70	6.70	9.20	9.20	15.30	15.30
Fittings	2.30	2.30	2.70	2.70	3.70	3.70
Hydrants	3.80	—	3 80	—	3.80	—
Line Valves	0.50	0.50	0 70	0.70	1.20	1.20
Service Conn.	11.00	—	11.00	—	11.00	—
Paving	5 10	5.10	5.10	5.10	5.10	5.10
Dewatering	1.20	1.20	1.20	1.20	1.20	1.20
Miscellaneous	4.40	2.90	4.90	3.40	5.90	4.70
Total Cost Per Linear Foot	$43.70	$27.40	$47.30	$31.00	$56.20	$40.20

Cost Category	16-inch		24-inch		30-inch	
	Dist	Trans.	Dist.	Trans.	Dist.	Trans.
Excavation	$ 9.70	$ 9.70	$ 11 50	$ 11.50	$ 12.30	$ 12.30
Pipe	23.20	23.20	38.00	38.00	55.40	55.40
Fittings	5.00	5.00	7.40	7 40	6.80	6.80
Hydrants	3.80	—	11.00	—	11.00	—
Line Valves	2.60	2.60	5.50	5.50	8.10	8.20
Service Conn.	11.00	—	11.00	—	11.00	—
Paving	5.75	5.75	8.80	8.80	9.40	9.40
Dewatering	1.25	1.25	1.25	1 25	1.40	1.40
Miscellaneous	8.00	6.50	12.75	11.25	15 10	13.60
Total Cost Per Linear Foot	$70.30	$54 00	$100 00	$83.70	$123.30	$107.10

NOTE: Costs were generated by Camp Dresser & McKee Inc. Costs include labor, design, and engineering services. Excavation costs will vary significantly depending on the depth of excavation and on the material that must be excavated. Distribution pipe costs are based on two service connections per 100 feet pipe laid. Costs will be lower in less densely settled areas.

bution mains have service connections and discharge outlets for fire hydrants, and they carry water relatively short distances from transmission mains to homes.) Table 26 lists costs for booster pump stations. To enable comparison of costs for different-sized water distribution extension projects, cost scenarios have been generated for communities of 10, 50 and 250 homes. These are shown in Tables 27 through 29. These distribution costs are lower than the costs listed in Table 25 because fewer connections are required to service homes. The first item listed on each of these tables, the 8-in transmission main, is usually the smallest of its type used.

Certain assumptions have been made in generating these cost scenarios. The distance between the existing distribution system and the communities was set at 10,000 ft; and amounts of transmission pipe needed were estimated from this distance. It was assumed that bridge crossings and highway piping work were not needed. Total costs would be different, of course, with different assumptions. If, for instance, the existing distribution system were closer to the communities in any of the three scenarios, say a half mile away, the cost of transmission piping would be reduced by nearly $232,000. Likewise, if a more severe terrain were assumed and bridge crossings and additional pump stations were required, the costs for these scenarios would be considerably higher. These factors and others such as head requirements and obtaining access to property through which the extension must pass complicate the decision of whether to extend existing water distribution systems and need to be carefully analyzed before making the final decision.

Table 26
Cost Breakdown for Booster Pump Stations

Cost Category	Brick Suction Lift		Pre-Fabricated Suction Lift	
	160 ft.	100 ft.	160 ft.	100 ft.
General Cleanup	7,400	6,100	7,400	6,100
Excav & Bkfill	1,900	1,900	1,900	1,900
Site Work	11,600	11,600	11,600	11,600
Concrete	4,100	4,100	4,100	4,100
Masonry	6,800	6,800	3,400	3,400
Carpentry	-	-	-	-
Process-Pump	30,700	28,200	30,700	28,200
Pump Controls	6,300	6,300	6,300	6,300
Instrumentation	30,000	30,000	30,000	30,000
Misc. Contract.	16,300	16,100	8,150	8,150
Misc. Hardware	9,900	9,900	9,900	9,900
Total Cost	$125,000	$121,000	$113,450	$109,650

[1] Costs are based on construction and installation of 1 MGD stations.

Table 27
Capital Costs of Water Distribution Extension for a Community of 10 Homes

Cost Category	Quantity	Unit Cost	Total Cost For Item
8-inch Transmission Main[1]	10,000 ft.	$31.00/ft.	$310,000
6-inch Distribution Main	3,000 ft.	$35.00/ft.[2]	$105,000
Stream Crossings	40 ft.	$60.00/ft.	$ 2,400
Booster Pump Station (Unnecessary)			
Storage Facility (Unnecessary)			
Subtotal			$417,400
Engineering Services & Contingency (30% of Subtotal)			$125,220
Total Cost			$542,620

Description: This cost scenario was generated for a 10 home community located about 2 miles (10,000 feet) from a suitable connection point to an existing water distribution system. It is assumed that 2-3 people live in each home and that each person uses 110 gallons of water per day—peak summer demand. The total water requirement for the 10 homes is approximately 0.0033 MGD. It is assumed that there is no significant increase in elevation, and therefore, a booster pump station is not needed to ensure adequate water supply. Because of the small size of the community, it is further assumed that water storage facilities (i.e., elevated tanks, earthen reservoirs) are unnecessary. Finally, it was assumed that there was one 40-foot stream crossing, but no bridge crossings (which at $200 + per foot can be prohibitively expensive).

Engineering services account for the design of the system; contingency covers unexpected costs during construction.

[1] The 8-inch pipe is generally the smallest transmission main used.

[2] Distribution pipe costs are lower than the costs listed in Table 25 because fewer connections are required to service homes.

Table 28
Capital Costs of Water Distribution Extension for a Community of 50 Homes

Cost Category	Quantity	Unit Cost	Total Cost For Item
8-inch Transmission Main[1]	10,000 ft.	$ 31.00/ft.	$310,000
6-inch Distribution Main	10,000 ft.	$ 36.00/ft.[2]	$360,000
Stream Crossings	40 ft.	$ 60.00/ft.	$ 2,400
Booster Pump Station		$110,000	$110,000
Storage Facility (Unnecessary)			
Subtotal			$782,400
Engineering Services & Contingency (30% of Subtotal)			$234,720

Total Cost	$1,017,120

Description: This cost scenario was generated for a 50 home community located about 2 miles (10,000 feet) from a suitable connection point to an existing water distribution system. It is assumed that 2-3 people live in each home and that each person uses 110 gallons of water per day—peak summer demand. The total water requirement for the 50 homes is approximately 0.02 MGD. It is assumed that there is a significant increase in elevation, requiring that a 1.0 MGD booster pump station be installed to provide adequate water supply. Because of the small size of the community, it is further assumed that water storage facilities are unnecessary. Finally, it was assumed that there was one 40-foot stream crossing.

[1] The 8-inch pipe is generally the smallest transmission main used.

[2] Distribution pipe costs are lower than the costs listed in Table 25 because there are fewer connections to homes.

Table 29
Capital Costs of Water Distribution Extension for a Community of 250 Homes

Cost Category	Quantity	Unit Cost	Total Cost For Item
8-inch Transmission Main[1]	10,000 ft.	$ 31.00/ft.	$310,000
6-inch Distribution Main	18,750 ft.	$ 43.00/ft.[2]	$806,250
Stream Crossings	40 ft.	$ 60.00/ft.	$ 2,400
Booster Pump Station		$110,000	$110,000
Storage Tank	100,000 gal.	$ 1.20/gal.	$120,000
Subtotal			$1,348,650
Engineering Services & Contingency (30% of Subtotal)			$404,595

Total Cost	$1,753,745

Description: This cost scenario was generated for a 250 home community located about 2 miles (10,000 feet) from a suitable connection point to an existing water distribution system. It is assumed that 2-3 people live in each home and that each person uses 110 gallons of water per day—peak summer demand. The total water requirement for the 250 homes is approximately 0.08 MGD. It is assumed that the community is large enough to require both a 1.0 MGD booster pump station and an elevated storage tank. Finally, it was assumed that there was one 40-foot stream crossing.

[1] The 8-inch pipe is generally the smallest transmission main used.

[2] Distribution pipe costs are lower than the costs listed in Table 25 because there are fewer connections to homes.

Limitations

Other than cost, there are few limitations to extending water distribution systems, because centralized systems have been used in cities and towns in the United States for over a hundred years. A well-established network of materials, manufacturers, engineers, and construction companies is capable of water distribution system installation. The most significant limitations are the obtaining of access to privately and publicly held land needed for transmission main installation and the problem of supplying homes with clean water while the distribution system is being designed and constructed. Most transmission mains are buried beneath road surfaces, allowing excavation equipment easy access for installation and maintenance. Instances may arise, however, when it is more practical or economical to install transmission mains in fields, lawns, and vacant lots. If these open areas are privately owned, a "right of way" (a legally binding agreement between the landowner and the water distribution authority) must be obtained, or when an agreement cannot be reached, a court order for "eminent domain" must be invoked. The process of obtaining rights of way and court orders can take months or even years to complete. To circumvent the process and avoid costly delays, the decision is often made to install the transmission main around the property or properties in question, even though this increases the costs of the system.

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Section 7
Index

skimmers, 19
trench method, 15, 16

GAC (granular activated carbon), 75, 77-87

Gasoline properties, 6,7

Gasoline removal from soils, 35-55
cost, 37, 40-42, 45, 47, 51-53
effectiveness, 35, 36, 39-40, 43-45, 47-53
enhanced volatilization, 38-41
excavation and disposal, 35-38
incineration, 42
soil venting, 42-45
soil washing/extraction, 45-47

Gasoline removal from groundwater, 57-98
mass transfer coefficient, 61-63
methods, 57

Henry's law, 61-63, 70

Hydrogen peroxide
control of fouling, 73
in biorestoration (saturated zone), 89
microbial degradation (unsaturated zone), 50
oxidation, 57

Incineration, 35, 42, 52-53

Ion exchange, 1-6

Iron
activated carbon, 67, 71, 74, 85
air stripping, 67, 71, 74

Microbial degradation (unsaturated zone), 35, 47-53

Onda equations, 62-63

Partition coefficients (gasoline), 9, 13

Point-of-entry treatment, 99-194
costs, 102-103
devices, 99
limitations, 114
systems, 100-101
use of carbon, 100-104

Pumping wells, 16-18
dual pump, 16-21, 27
single pump, 16-18, 27

Resin adsorption, 57

Reverse osmosis, 57, 99-100

Soil venting, 35, 42-45, 52-53

Soil washing, 35, 45-47, 52-53

Stripping factor, 63

Structure of subsurface
capillary zone, 6, 9-10
saturated zone, 8, 10-11
unsaturated zone, 5-10, 12, 13

Trench method, 15-18

Ultraviolet irradiation, 57

Volatilization, 9, 38-40