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# Soil Remediation Techniques at Uncontrolled Hazardous Waste Sites

## A Critical Review

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The objective of this critical review is to address soil remediation techniques at uncontrolled hazardous waste sites with regard to the following areas: 1) important regulatory and technical issues and information needs concerning soil remediation at uncontrolled hazardous waste sites; 2) approaches for selection of remediation techniques; and 3) the current state of knowledge regarding soil remediation techniques, including applications and limitations. The areas identified above are addressed with regard to current information, selected milestone publications, and specific applications of technologies to provide a synthesis of the topic.

The information concerning current issues, approaches, and soil remediation techniques presented was critically reviewed in order to: 1) identify deficiencies in current approaches; 2) develop a conceptual framework for remediation; and 3) recommend improved approaches for selection of remediation technologies.

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In 1980 the first comprehensive federal law addressing releases of hazardous substances into the environment was enacted, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or Superfund. The primary goal of CERCLA was to establish a mechanism to respond to releases of hazardous substances at abandoned or uncontrolled hazardous waste sites that posed a threat to human health and the environment. The regulatory framework for guiding both short-term emergency responses as well as long-term cleanup of hazardous waste sites became the National Contingency Plan (NCP), revised in 1982 and 1985. Under CERCLA, the NCP outlined the level of cleanup necessary at a Superfund site and established procedures to be followed for discovery, response, and remediation of a hazardous waste site.<sup>1</sup>

The Superfund Amendments and Reauthorization Act of 1986 (SARA), Section 121, Cleanup Standards, stipulates rules for selection of remedial actions, provides for review of those actions, describes requirements for the degree of cleanup, and mandates conformance with the NCP whenever possible.<sup>2</sup> Under Section 121, the U.S. Environmental Protection Agency (U.S. EPA) is required to select remedial actions involving treatment that "... permanently and significantly reduces the volume, toxicity, or mobility of haz-

ardous substances, pollutants, and contaminants..." The U.S. EPA must also approve the selection of a remedial action that is "protective of human health and the environment, that is cost-effective, and that utilizes permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable."<sup>2</sup> Remedial actions also must meet all applicable or relevant and appropriate requirements (ARARs). Applicable requirements refer to standards, requirements, criteria, or limitations that specifically address a hazardous subsurface, pollutant, contaminant, remedial action, location, or other circumstance at a CERCLA site. Relevant and appropriate requirements refer to those cleanup standards that, although not applicable, address problems or situations sufficiently similar to those encountered at the site so that their use is suitable. Although SARA provides specific approaches to hazardous waste site remediation, because of the variety of releases and threats encountered at hazardous waste sites, specific remedial actions and cleanup levels must be determined on a site-by-site basis.<sup>3</sup>

In the proposed revision of the NCP,<sup>4</sup> the U.S. EPA addresses the need for rapid characterization of site risk and for evaluation of remedial actions through an approach that addresses site characterization and evaluation of remediation alternatives using a five-step process. The five-step process includes: 1) project scoping, 2) remedial investigation, 3) feasibility study, 4) selection of an action, and 5) documentation.

Project scoping involves a preliminary site characterization and the development of remedial investigation and feasibility studies (RI/FS), and also addresses quality and quantity aspects of data collection. Remedial investigation involves data gathering related to site characterization and selection of response actions. In one major effort to guide site characterization activities so that they relate more efficiently to selection of surface and subsurface remediation technologies, the U.S. EPA offered a seminar on site characterization for subsurface remediations through the Robert S. Kerr Environmental Research Laboratory (RSKERL),<sup>5</sup> with a follow-up publication of the same title.<sup>6</sup> The RSKERL has also developed specific technology transfer information through the Subsurface Remediation Technology Support Center.<sup>7</sup>

The feasibility study involves analyzing remedial alternatives for a specific site related to effectiveness, ease of implementation, and cost. Treatment technologies that meet the above requirements are selected and are further evaluated based on nine criteria mandated by CERCLA and SARA, including: 1) overall protection of human health and the environment; 2) compliance with applicable or relevant and appropriate requirements (ARARs); 3) long-term effectiveness and permanence; 4) reduction of toxicity, mobility, or volume; 5) short-term effectiveness; 6) implementability; 7) cost; 8) state acceptance; and 9) community acceptance.<sup>3</sup>

The nine criteria cited above are used in the preparation of the record of decision (ROD) and have been organized into three groups: 1) threshold, 2) balancing, and 3) modifying criteria. Threshold criteria that must be met include protection of human health and the environment and compliance with ARARs. Balancing factors are used to weigh major tradeoffs among viable approaches and include long-term effectiveness and permanence; reduction of toxicity, mobility, or volume; short-term effectiveness; implementability; and cost. Modifying criteria include state and community acceptance considerations. The final phase of the remedial action process involves documenting how the nine criteria were used to select the chosen remedial technology in a ROD.<sup>3</sup>

Two major problems with regard to meeting soil remediation requirements under CERCLA have been: 1) lack of availability of appropriate technologies, and 2) lack of methods and approaches for evaluating and selecting remedial technologies for specific site-waste scenarios, especially with regard to in situ remediation.

Recognition for the need for development of technologies and for communication of the types of technologies developed to the user community, as well as applications and limitations of the technologies, was identified in SARA (1986). For the first time SARA directed the U.S. EPA to use Superfund monies to conduct research and technology transfer to support the cleanup of sites on the National Priorities List. In 1986, the U.S. EPA Office of Solid Waste and Emergency Response (OSWER) and Office of Research and Development (ORD) established the Superfund Innovative Technology Evaluation (SITE) program to promote the development and use of innovative technologies to clean up Superfund sites, composed of three related programs: 1) demonstration program; 2) emerging technologies program; and 3) measurement and monitoring technologies program.<sup>8</sup>

As an extension of the SITE program, the U.S. EPA is participating in an international study on "Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater." The study offers an opportunity to obtain a data base on various remedial action unit processes without any single country having to commit a disproportionate amount of its internal resources to any specific activity.<sup>9</sup> Each participating country provides the necessary resources for the demonstrations it is sponsoring. The study is a five-year program, with participants from Canada, Den-

mark, Federal Republic of Germany, France, Greece, Italy, Japan, the Netherlands, Norway, Spain, and the United States.<sup>10</sup>

Since the need for cost-effective remedial action technologies for hazardous waste sites is a problem of all industrialized countries, several other international conferences are also held periodically concerning international experiences in remediation of contaminated soils.<sup>11-16</sup>

The U.S. EPA is sponsoring an additional program to identify and assess international technologies applicable to hazardous waste site remediation in the United States.<sup>17</sup> In Phase I of the study, of 95 technologies selected as potentially applicable to remediation of Superfund sites, 47 were identified as potentially applicable for soil remediation. Fact sheets, which include information on purpose and applicability, performance, limitations, economics, and status, have been developed for each international technology selected.<sup>18</sup>

In April, 1987, OSWER and ORD disseminated the U.S. EPA's first office-wide "Technology Transfer Strategy."<sup>19</sup> As part of this strategy, four Technology Support Centers were established at ORD laboratories in the areas of: 1) engineering and treatment; 2) ground water fate and transport; 3) monitoring and site characterization; and 4) exposure monitoring and ecological risk assessment. This integration of OSWER and ORD functions related to Superfund provided a foundation and a framework for the development and communication of specific approaches and technologies for hazardous waste contaminated sites.

Lack of methods and approaches for evaluating and selecting remedial technologies for site-specific scenarios represents a current major deficiency in the area of subsurface remediation, including soil remediation. In this paper the author proposes a rational approach for evaluating and selecting remedial technologies that incorporates new technologies as they become available to the user community.

### Technical Issues

The vadose zone is the region extending from the ground surface of the earth to the upper surface of the principal water-bearing formation, and is divided into three belts. The uppermost belt consists of soil and other materials that lie near enough to the surface to discharge water into the atmosphere in perceptible quantities by the action of plants or by soil evaporation and convection. The lowest belt, the capillary fringe, is located immediately above the water table and contains water drawn up from the zone of saturation by capillary action. The intermediate belt lies between the belt of soil water and the capillary fringe.<sup>20</sup> This paper addresses remediation of the uppermost belt of the vadose zone, and situations where the saturated zone is engineered to become unsaturated, e.g., when ground water is pumped out to create an unsaturated zone.

Technical issues directly related to the regulatory history and requirements for soil remediation techniques at uncontrolled hazardous waste sites involve understanding the physical, chemical, and biological processes involved in a waste/soil/site system. Specific technical issues identified and selected by the author as "critical issues" for addressing in this review include:

- Conceptual approach for proposed soil remediation;
- Soil processes that affect remediation techniques;
- Site characterization factors for selection of remediation techniques;
- Treatment approaches;
- Remediation techniques for contaminated soils;
- Additional issues and research needs

The technical issues identified above will be addressed individually.

Remediation of contaminated soils generally is accomplished by using one or more of three types of systems: 1) in situ, 2) prepared bed, and 3) in-tank reactor.<sup>3,21-31</sup>

An in situ treatment system consists of treating contaminated soil in place, where the contamination is located, i.e., the contaminated soil is not moved from the ground. Milestone publications containing scientific and engineering information specifically addressing in situ treatment include: "Review of In-Place Treatment Techniques for Contaminated Surface Soils, Volume 1: Technical Evaluation and Volume 2: Background Information for In Situ Treatment,"<sup>23-24</sup> an update of Volume 1, "Handbook on In Situ Treatment of Hazardous Waste-Contaminated Soils,"<sup>3</sup> "Bioremediation of Contaminated Surface Soils,"<sup>22</sup> and "In Situ Biological Treatment of Hazardous Waste-Contaminated Soils."<sup>32</sup>

In a prepared bed system, the contaminated soil may be either: 1) physically moved from its original site to a newly prepared area, which has been designed to enhance treatment and/or to prevent transport of contaminants from the site; or 2) removed from the site to a storage area while the original location is prepared for use, then returned to the bed, where treatment is accomplished. Preparation of the bed may consist of such activities as placement of a clay or plastic liner to retard transport of contaminants from the site, or addition of uncontaminated soil to provide additional treatment medium. Treatment may be enhanced with biological and/or physical/chemical methods, as with in situ systems.<sup>22</sup> Prepared bed treatment approaches are based on modifications of principles developed in the area of land application of solid and liquid wastes, and in the area of land treatment of hazardous wastes.<sup>22,33-34</sup> In-tank treatment systems are used for treatment of contaminated soil, where the soil is physically removed and placed in an enclosed reactor based upon batch, complete mix, or plug flow systems commonly used in chemical and environmental engineering systems; the soil may be in an unsaturated or a saturated physical form. Common tank treatment systems include composting, slurry-phase treatment, and solid-phase treatment.<sup>26</sup>

## Conceptual Approach Proposed for Soil Remediation

### The Chemical Mass Balance

A conceptual framework for soil remediation technique evaluation, selection, and monitoring is proposed, based on a critical review and evaluation of current information and activities employed at hazardous waste sites. The conceptual framework is the chemical mass balance, the cornerstone of science and engineering research and industry. The concept of a chemical mass balance is familiar to professionals trained in the physical or life sciences or in engineering. In contrast to obtaining quantitative accuracy regarding the amount of contaminants initially present at an uncontrolled site, the chemical mass balance provides a rational and fundamental basis for asking specific questions and obtaining specific information that is necessary for determining fate and behavior, for evaluating and selecting treatment options, and for monitoring treatment effectiveness at both laboratory scale and at field scale. While a mass balance, or materials balance, is routinely conducted on above-ground treatment processes,<sup>35-38</sup> and for groundwater processes,<sup>39-40</sup> a mass balance approach has generally not been applied to the subsurface-surface system to link characterization and treatment. The information needed to construct a mass balance for contamination at a site simultaneously addresses site characterization and remediation.

Using the chemical mass balance approach, a methodology was developed by the author for integrating data collection activities at CERCLA sites in order to address simultaneous site characterization and remediation technique selection. The proposed methodology consists of four elements: 1) characterization, 2) assessment of the problem, 3) treatment (train) selection, and 4) monitoring treatment performance. The first step involves characterization in the context of waste/soil/site interactions to address the question "Where is the contamination and in what form(s) does it exist?" The second step, assessment of the problem, utilizes subsurface fate and behavior information to address the question, "Where is the contamination going under the influence of natural processes?" The problem can be defined in the context of mobility versus degradation for chemicals at a site. Using mathematical models or other tools, the chemicals can be ranked in order of their relative tendencies to leach, to volatilize, and to remain in-place under site-specific conditions. Containment and/or treatment options can then be selected that are chemical-specific and that address specific escape and attenuation pathways (third step). Treatment trains can be selected to address specific waste phases at specific times during remediation (volatile, leachate, solid phase, pure product), with the selection based upon results of a mass balance evaluation through time to identify the fate of each waste phase. Finally monitoring programs can be designed for specific chemicals in specific phases in the subsurface at specific times (fourth step). The approach for using the methodology consists in applying a mass balance for each element of the methodology. This approach assists in the collection of specific information that is transferrable among all four elements of the methodology, and also addresses the technical issues of soil remediation within the context of regulatory goals.

## Soil Processes that Affect Remediation Techniques

The soil environment at a contaminated site is illustrated in Figure 1. The contaminated soil is a system generally consisting of four phases: 1) aqueous; 2) gas; 3) oil (commonly referred to as non-aqueous phase liquid, or NAPL); and 4) solid, which has two components, an inorganic mineral compartment and an organic matter compartment.<sup>22</sup>

### Distribution of Waste Constituents

Interphase transfer potential for waste constituents among oil (waste or NAPL), water, air, and solid (organic and inorganic) phases of a soil system is affected by the relative affinity of the waste constituents for each phase, and may be quantified through calculation of partition coefficients.<sup>34,41-42</sup> Distribution coefficients are calculated as the ratio of the concentration of a chemical in the soil (aquifer), oil, or air phase to the concentration of a chemical in the water phase. A waste chemical, depending on its tendency to be associated with each phase, will distribute itself among the phases, and can be quantified in terms of distribution coefficients. Distribution coefficients are available for a variety of chemicals and can be expressed as ratios of the concentrations of a chemical between two phases in the subsurface:

$$K_d = \text{Concentration in solid phase} / \text{Concentration in aqueous phase}$$

$$K_o = \text{Concentration in oil phase} / \text{Concentration in aqueous phase}$$

$K_h$  = Concentration in air phase/Concentration in aqueous phase

$K_h$  is also known as Henry's law constant. When distribution coefficients are not available, they can be estimated using structure-activity relationships (SARs) or can be determined in laboratory tests.<sup>41</sup>

Concerning toxic metal contamination of soils, metal concentrations in the soil aqueous phase are governed by the following interrelated processes: 1) inorganic/organic complexation; 2) acid-base reactions; 3) redox reactions; 4) precipitation/dissolution reactions; and 5) interfacial reactions. The ability to predict the concentration of a given toxic metal in the soil solution depends, to a large degree, on the accuracy with which the multiphase equilibria can be calculated, evaluated, or predicted.<sup>24</sup> Arsenic, selenium, and chromium are metals that can exist as anions. Because of their anionic nature, their behavior in soil will differ from other toxic metals. However, since metals distribute among the phases of the soil systems described previously, distribution coefficients may be used, along with metal speciation, to evaluate metal distribution in a contaminated soil system.

The partition coefficient of a chemical between soil and water is given by:

$$K_d = C_s/C_w \quad (1)$$

where  $K_d$  is the soil/water partition coefficient (unitless if  $C_s$  and  $C_w$  are in the same units),  $C_s$  is the concentration of chemical in the soil phase, and  $C_w$  is the concentration of chemical in the aqueous phase.

$K_d$  values for a soil can be estimated from  $K_{oc}$  values if the organic fraction for the soil,  $f_{oc}$ , is known, assuming that hydrophobic interactions dominate:

$$K_d = K_{oc}f_{oc} \quad (2)$$

where  $K_{oc}$  is the organic carbon normalized soil/water partition coefficient. Other approaches for determining  $K_{oc}$  values have been investigated by Sims et al.<sup>41</sup> and Sabljic.<sup>43-44</sup>

The partition coefficient of a chemical between water and oil is given by:

$$K_o = C_o/C_w \quad (3)$$

where  $K_o$  is the oil/water partition coefficient (unitless if  $C_o$  and  $C_w$  are in the same units),  $C_o$  is the concentration of chemical in the oil phase, and  $C_w$  is the concentration of chemical in the water phase. Methods for estimating values for  $K_o$  are presented by Leo and Hansch.<sup>45</sup>

The partition coefficient of a chemical between air and water can be written as:

$$K_h = C_a/C_w \quad (4)$$

where  $K_h$  is the air/water partition coefficient,  $C_a$  is the concentration of chemical in the air phase, and  $C_w$  is the concentration of chemical in the aqueous phase.  $K_h$  can also be expressed as a dimensionless Henry's Law constant,  $H/R.T.$  Methods for calculating  $K_h$  values are presented by Sims et al.<sup>41</sup>

#### Transport of Waste Constituents

Retardation of the downward transport (leaching potential) and upward transport (volatilization potential) is referred to as immobilization of waste constituents. Immobilization of organic chemicals has been related to the soil organic matter content (especially for hydrophobic chemicals),<sup>46</sup> soil moisture,<sup>47</sup> and presence of concentration of organic solvents.<sup>48-49</sup>

A means of predicting rate of transport of a constituent through a subsurface system is to describe its mobility (or relative immobility) by predicting its retardation.<sup>48,50</sup> Retardation is a factor that describes the relative velocity of the constituent compared to the rate of movement of water through the subsurface, i.e.,:

$$R = V_w/V_c \quad (5)$$

where  $R$  = retardation factor;  $V_w$  = average water velocity; and  $V_c$  = average constituent velocity. A retardation factor greater than one indicates that a constituent is moving more slowly than water through a system. A factor developed from a transport model combined with a description of sorption processes, as defined by a linear Freundlich isotherm,<sup>24,28</sup> can be calculated from the following equation for retardation in unsaturated soil:

$$R = 1 + (\rho K_d/\theta) \quad (6)$$

where  $\rho$  = soil bulk density;  $K_d$  = soil water partition coefficient, which describes the partitioning between the soil solid phase and soil water; and  $\theta$  = volumetric moisture content. For a saturated system,  $\theta$  is replaced by the porosity of the system.

This information can be used to evaluate treatment techniques for a contaminated soil system (e.g., through control of soil moisture, changes in bulk density, or addition of amendments to the soil that will affect soil water partition coefficients) so that constituents can be "captured" or contained within the system, thus allowing time for degradation at the site or for engineering implementation and performance of other remediation treatment techniques, such as soil washing.<sup>22</sup>

Linear retardation of chemicals in the vapor phase can be expressed as:

$$R = 1 + P_b K_p/O_A K_h + O_w/O_A K_h \quad (7)$$

where  $P_b$  is bulk density,  $K_p$  and  $K_h$  represent partition coefficients between soil and water and between air and water, respectively, and  $O_A$  and  $O_w$  represent air and water content, respectively. The second term in the equation represents partitioning into soil organic matter, and the third term represents partitioning in soil water.<sup>51</sup> Aqueous and vapor phase partitioning have been evaluated for hydrocarbons by Baehr<sup>52</sup> and by Kraemer et al.<sup>53</sup> in the unsaturated zone.

Immobilization of constituents in in situ, prepared bed, and in-tank treatment systems generally is measured through a leaching or emissions measurement procedure to determine the potential for release from the matrix. Specific immobilization remediation technologies are discussed in a subsequent section of this paper.

#### Reaction of Waste Constituents

**Degradation.** Each phase in Figure 1 can also be a site for biological and/or abiotic (chemical) reactions that result in the transformation of a parent chemical and therefore destruction of the parent chemical. Characterization of the reaction (degradation) of specific chemicals in the waste/soil mixture is important to evaluate the assimilative capacity of the site for each chemical.

Degradation of most organic compounds in subsurface systems may be described by monitoring their disappearance through time. Disappearance, or rate of degradation, is often expressed as a function of the concentration of one or more of the constituents being degraded. This is termed the order of the reaction and is the value of the exponential used to describe the reaction.<sup>54</sup> Zero and first order power rate models are often used in studies of the degradation of organic chemicals in soil systems.

Zero order reactions are ones in which the rate of transformation of an organic constituent is unaffected by changes in the constituent concentration because the reaction rate is determined by some other factor than the constituent concentration. If a constituent  $C$  is transformed to  $X$ , the rate of change of  $C$  is:

$$dC/dt = -k \quad (8)$$

On integration, the equation becomes:

$$C_t = C_o - kt \quad (9)$$

where  $C_t$  = concentration of constituent remaining at time  $t$ ; and  $C_o$  = initial concentration of constituent, and  $k$  = zero order rate constant. A useful term to describe reaction kinetics is the half-life,  $t_{1/2}$ , which is the time required to transform 50 percent of the initial constituent:

$$C_t = C_o/2, \text{ then } t_{1/2} = C_o/2k \quad (10)$$

The first order rate model is widely used because of its effectiveness in describing observed results as well as its inherent simplicity. Its use also allows comparison of results obtained from different studies. In a first order rate reaction, the rate of transformation of a constituent is proportional to the constituent concentration:

$$dC/dt = -kC \quad (11)$$

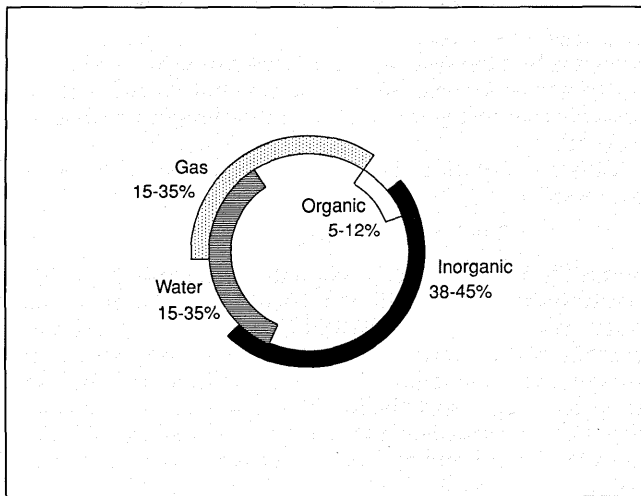


Figure 1. Typical volumetric composition of soil.<sup>22</sup>

where  $C$  = contaminant concentration (mass/mass);  $t$  = time; and  $k$  = first order rate constant (1/time). After integration of this equation and rearrangement of the integrated equation, the following equation may be used to graphically determine the rate constant,  $k$ :

$$\ln(C_t/C_o) = -kt \quad (12)$$

where  $C_t$  = concentration of constituent remaining at time  $t$ ; and  $C_o$  = initial concentration of constituent. A plot of  $\ln(C_t/C_o)$  versus  $t$  is linear with a slope of  $-k$ . The rate constant  $k$  is independent of the concentration of constituent, since the slope is constant over time. To calculate the time required to transform one-half of the initial constituent ( $C_t = C/2$ ), the following equation is used:

$$\ln[(C_o/2)/(C_o)] = -kt_{1/2} \quad (13)$$

which is equal to:

$$t_{1/2} = 0.693/k \quad (14)$$

where  $t_{1/2}$  = half-life of the constituent.

First order kinetics generally apply when the concentration of the compound being degraded is low relative to the biological activity in the subsurface. However, very low concentrations may be insufficient to initiate enzyme induction or support maintenance requirements necessary for microbial growth, even if the compound can be used as an energy source.<sup>55</sup>

Another model used to describe degradation in the subsurface is the hyperbolic rate model, which is similar to

Michaelis-Menten enzyme kinetics. This model is expressed as:

$$dC/dt = -k_1C/k_2 + C \quad (15)$$

where  $k_1$  and  $k_2$  are constants. The constant  $k_1$  represents the maximum rate of degradation that is approached as the concentration increases. This model simulates a catalytic process in which degradation may be catalyzed by microorganisms.

Often an organic compound that cannot be used as a sole carbon and energy source for microorganisms is degraded. Biodegradation of the compound does not lead to energy production or cell growth. This biodegradation process is referred to as cometabolism,<sup>56</sup> or cooxidation if the transformation involves an oxidation reaction.<sup>57</sup> Cometabolism occurs when an enzyme produced by an organism to degrade one substance that supports growth also degrades another nongrowth substrate that is neither essential for, nor sufficient to, support microbial growth. The nongrowth substrate is only incompletely oxidized, or otherwise transformed, by the microorganism involved, although other microorganisms may utilize by-products of the cometabolic process. Keck et al.<sup>58</sup> summarized findings that indicated that a variety of naturally occurring microorganisms can utilize a variety of aliphatic and aromatic compounds as carbon and energy substrates for achieving cooxidation of straight chain and aromatic hydrocarbon compounds. In a soil where toxic conditions do not prevent microbial activity, cooxidation or cometabolism may be expected to be readily occurring in environments containing similar chemical substances. Cooxidation may be a prerequisite for the mineralization of many recalcitrant substances found in the soil and ground water subsurface environment, such as polynuclear aromatic hydrocarbons.

To assess the potential for biological degradation at a specific contaminated site, the use of studies incorporating materials balance and mineralization approaches to determine the environmental fate and behavior of the constituents in the specific soil is recommended (Table I).<sup>59</sup> Rate of degradation is calculated by measuring the loss of parent compound and the production of carbon dioxide with time of treatment, as well as production and disappearance of intermediate products. Abiotic controls are also used in order to evaluate the mechanism(s) of degradation. Results can be reported, for example, as rate/extent of biological degradation corrected for volatilization and for abiotic loss.<sup>34</sup>

Table I. Materials balances and mineralization approaches to biodegradation assessment.<sup>59</sup>

Biodegradation approach	Process examined
Materials balances	Recovery of parent compound in the air, soil water, and soil solids (extractable) Recovery of transformation products in the air, soil water, and soil solids (extractable)
Mineralization	Production of carbon dioxide, and/or methane from the parent compound Release of substituent groups, e.g., chloride or bromide ions

*Transformation/detoxification.* Transformation refers to the partial alteration of hazardous constituents into intermediate products. Intermediate products may be less toxic or more toxic than the parent compound, and therefore the rate and extent of detoxification of the contaminated mate-

rial should be evaluated.<sup>60-62</sup> For example, the degradation pathway of the single chlorinated compound, trichloroethylene (TCE) leads to the production of six chlorinated volatile hydrocarbons. The degradation of tetrachloroethylene (PCE) leads to the production of seven chlorinated volatile hydrocarbons, while the degradation of 1,1,1-trichloroethane (1,1,1-TCA) leads to the production of four chlorinated hydrocarbons. Two of the metabolic products formed, vinyl chloride and 1,1-dichloroethane (1,1-DCA), have been classified as a carcinogen and a probable carcinogen, respectively.<sup>63</sup> Vinyl chloride is the most persistent of the compounds under anaerobic conditions, but can be rapidly degraded under aerobic conditions.<sup>64-65</sup> Management of a bioremediation system to accomplish treatment of these compounds in a manner such as to protect human health and the environment should incorporate considerations of detoxification of parent compounds as well as their disappearance. For these halogenated organic compounds, a bioremediation system could possibly consist of maintenance of an anaerobic environment followed by aeration, after anaerobic degradative processes have reduced the levels of parent compounds to acceptable levels.

To assess detoxification, bioassays may be used to quantify toxicity by measuring the effect of a chemical on a test species under specified test conditions.<sup>42</sup> The toxicity of a chemical is proportional to the severity of the chemical on the monitored response of the test organism(s). Toxicity assays utilize test species that include rats, fish, invertebrates, microorganisms, and seeds. The assays may utilize single or multiple species of test organisms. The use of a single bioassay procedure does not provide a comprehensive evaluation of the toxicity of a chemical in a soil/chemical-impacted system. Often a battery of bioassays is utilized that may include measurements of effects on general microbial activity (e.g., respiration, dehydrogenase activity) as well as assays relating to activity of subgroups of the microbial community (e.g., nitrification, nitrogen fixation, cellulose decomposition). Bioassays utilizing organisms from different ecological trophic levels may also be used to determine toxicological effects. However, use of a single assay as a screening test to identify relative toxicity reduction in the environment is a commonly used procedure. Assays using microorganisms are often used due to their speed, simplicity, ease in handling, cost effectiveness, and use of a statistically significant number of test organisms that is required to detect the effects of potentially toxic materials in the environment.<sup>66-67</sup>

Two microbial bioassays that have been used to evaluate toxicity of wastes in soil systems are the Ames *Salmonella typhimurium* mammalian microsome assay and the Microtox™ test system. The Ames assay is a measure of the mutagenic potential of hazardous compounds<sup>68-69</sup> and has been widely used to evaluate environmental samples.<sup>62,70-73</sup> A high correlation has been shown between carcinogenicity and mutagenicity, where about 90 percent of known carcinogens tested mutagenic in the Ames assay.<sup>74</sup> Special strains of *Salmonella typhimurium* that require histidine to grow are used to test for mutagenicity. When plated on a histidine-free medium, the only bacteria able to form colonies are those that have reverted to the "wild" state and are able to produce their own histidine. Without the addition of test chemicals, this back mutation occurs at a rate specific to each strain type (spontaneous reversion rate). The addition of chemicals that are mutagenic increases the reversion rate. Several dose levels of a chemical, mixture of chemicals, or an environmental sample are added to obtain a dose response. Some mutagens act directly on the bacterial cells while others require activation by mammalian microsomes. These microsomes are generally obtained from liver extracts of Aroclor 1254-induced rats (i.e., rats injected with the polychlorinated biphenyl (PCB), Aroclor 1254). The extract, referred to as the S-9 fraction, contains enzymes that meta-

bolically convert certain chemicals to active mutagens, simulating the activity that occurs in living mammalian systems. Several strains of *Salmonella typhimurium* have been developed in order to detect different types of mutagens. The recommended strains for general mutagenicity testing include TA97, TA98, TA100 and TA102. TA97 and TA98 detect frameshift mutagens. TA100 detects mutagens causing base-pair substitutions, while TA102 detects a variety of mutagens not detected by the other strains.

The Microtox™ assay is an aqueous general toxicity assay that measures the reduction in light output produced by a suspension of marine luminescent bacteria in response to an environmental sample.<sup>75</sup> Bioluminescence of the test organism depends on a complex chain of biochemical reactions. Chemical inhibition of any of the biochemical reactions causes a reduction in bacterial luminescence. Therefore, the Microtox™ test considers the physiological effect of a toxicant and not just mortality. Matthews and Bulich<sup>76</sup> described a method of using the Microtox™ assay to predict the land treatability of hazardous organic wastes. Matthews and Hastings<sup>77</sup> developed a method using the Microtox™ assay to determine an appropriate range of waste application loading for soil-based treatment systems. Symons and Sims<sup>61</sup> utilized the assay to assess the detoxification of a complex petroleum waste in a soil environment. The assay was also included as a recommended bioassay in the U.S. EPA *Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations*.<sup>34</sup>

**Abiotic reactions.** Measurement of physical abiotic loss mechanisms and partitioning of organic substances into air as well as soil phases, i.e., conducting a mass balance, should be used in degradation studies to ensure that information generated is related to the disappearance mechanisms of the constituents in the soil system.<sup>78-79</sup> This type of information is needed in order to more accurately evaluate and select treatment techniques. For example, for organophosphorus pesticides, sorption-catalyzed hydrolysis of ester linkages is known to be important in influencing degradation in soil. An understanding of abiotic reactions as influenced by sorption and pH of the system may allow the design of a more effective remediation strategy. If abiotic controls are not used, the disappearance of a chemical may be attributed solely to biological activity, though biological activity may not play the major role in the degradation of the chemical. Therefore, knowledge of the reaction mechanism is directly related to efficiency and effectiveness in designing remediation strategies and selecting remediation techniques.

## Summary

The soil and subsurface processes described above, combined with information concerning the movement of fluids (gases, aqueous phase, and pure product flow) in the unsaturated and saturated zones, provide the inputs into the chemical mass balance that can be used for characterizing a site, for assessing the problem of mobility, for evaluating treatment techniques, and for identifying chemicals in specific phases for monitoring treatment effectiveness.

## Site Characterization Factors for Soil Remediation Techniques

### Extent and Magnitude of Contamination

Wastewater has historically been characterized in terms of its interaction and potential impact on the assimilative capacity of surface water receiver systems, generally rivers or lakes (e.g., requiring measurement of characteristics such as oxygen-demanding substances and levels of substances toxic to aquatic organisms). However a surface and subsurface-based waste characterization program at a hazardous waste

**Table II.** Soil-based waste characterization.<sup>24</sup>

<b>Chemical class</b>	
Acid	
Base	
Polar neutral	
Nonpolar neutral	
Inorganic	
<b>Chemical properties</b>	
Molecular weight	
Melting point	
Specific gravity	
Structure	
Water solubility	
<b>Chemical reactivity</b>	
Oxidation	
Reduction	
Hydrolysis	
Precipitation	
Polymerization	
<b>Soil sorption parameters</b>	
Freundlich sorption constants (K, N)	
Sorption based on organic carbon content ( $K_{oc}$ )	
Octanol-water partition coefficient ( $K_{ow}$ )	
<b>Soil degradation parameters</b>	
Half-life ( $t_{1/2}$ )	
Rate constant (first order)	
Relative biodegradability	
<b>Soil volatilization parameters</b>	
Vapor pressure	
Henry's law constant	
Sorption based on organic carbon content ( $K_{oc}$ )	
Water solubility	
<b>Soil contamination parameters</b>	
Concentration in soil	
Depth of contamination	
Date of contamination	

site addresses the vadose zone and ground water as the receiver system (e.g., requiring measurement of characteristics that reflect individual chemical mobility and destruction in the subsurface environment and those that affect human health as well as environmental toxicity); it also describes the behavioral interaction of waste chemicals in each surface and subsurface phase.

The identification of waste sources by soil phases, i.e., identification and amount (if possible) of waste constituents associated with each phase, allows an assessment of the magnitude (mass) and physical form(s) of waste that must be treated (e.g., aqueous, gas, oil (NAPL), and solid fractions), and comprises the first step in the mass balance characterization of waste sources at a site.

Specific site characteristics important for describing and assessing the environmental behavior and fate for organic constituents in the soil and subsurface are listed in Table II. For each chemical, or chemical class, information required can be summarized as: 1) characteristics related to potential leaching, e.g., water solubility, octanol/water partition coefficient, solid sorption coefficient; 2) characteristics related to potential volatilization, (e.g., vapor pressure, relative volatilization index); 3) characteristics related to potential degradation, (e.g., half-life, degradation rate, degradability index); and 4) characteristics related to chemical reactivity, (e.g., hydrolysis half-life, soil redox potential).<sup>24</sup> The information presented in Table II is also used for assessing the problem(s) at a site and for the evaluation and selection of containment/treatment management options.

The U.S. EPA has developed guidance concerning critical site-specific characterization requirements for use of specific remediation technologies for clean-up of contaminated soils.<sup>80</sup> These characterization parameters are presented for biological treatment technologies, physical/chemical treatment technologies, immobilization technologies, thermal treatment technologies, and in situ treatment technologies in Tables III, IV, V, VI, and VII, respectively.

Determination of the distribution of waste chemicals among phases that comprise the soil and subsurface at a site

**Table III.** Characterization parameters for biological treatment techniques.<sup>80</sup>

Treatment technique	Parameter	Purpose and comments
General	<b>Physical:</b>	
	Moisture content	To determine the treatability of the material and the treatment process of choice.
	Field capacity	
	pH	
	Temperature	
	Oxygen availability	
	<b>Chemical:</b>	
	Total Organic carbon (TOC)	To determine the treatability of the material and the treatment process of choice.
	Redox potential	
	Carbon:nitrogen:phosphorus ratio	To determine mineral nutrient requirements.
	<b>Biological:</b>	
	Soil incubation tests	To determine biodegradation potentials and to quantify biodegradation rates of contaminants.
	Electrolytic respirometer tests	To measure oxygen uptake and biodegradation.
Culture studies	To determine the indigenous microflora or specifically adapted microflora to be used in the inoculum during enrichment procedures.	
Bacterial enumeration tests (e.g., spread-plate techniques)	To determine the bacterial population density in the inoculum.	
Microbial toxicity/growth inhibition tests	To determine biological activity in the laboratory.	



indicates potential pathways of transport, or escape, from a site. Through a determination of subsurface flow conditions as part of site characterization activities (aqueous, gas, and pure product flow in the vadose zone and aqueous plume and pure product movement in the saturated zone), an assessment of the mass of material moving through a site and potential movement off-site can be made:

$$\text{concentration (mass/vol)} \times \text{rate of flow (vol/time)} = \text{mass flow at site (mass/time)} \quad (16)$$

This information is combined with additional information, discussed in the next section, that is needed for assessment

of the problem(s) with respect to treatment technique selection.

The U.S. EPA RSKERL, as part of its Superfund Technology Support Center Program activities, provides assistance to U.S. EPA regional offices and state regulatory agencies concerning appropriate site characterization activities at Superfund sites and other uncontrolled hazardous waste sites to support selection of effective remediation technologies. Examples of recommended site evaluation and characterization actions as related to the use of soils and the subsurface as the receiver system at uncontrolled hazardous waste sites are presented in Table VIII.

**Table IV.** Characterization parameters for physical/chemical treatment techniques.<sup>80</sup>

Treatment technique	Parameter	Purpose and comments
General	<b>Physical:</b> Type, size of debris	To determine need for pretreatment.
	Dioxins/furans, radionuclides, asbestos	To determine special waste-handling procedures.
Extraction -Aqueous -Solvent -Critical fluid -Air/steam	<b>Physical:</b> Particle-size distribution	To determine volume reduction potential, pretreatment needs, solid/liquid separability.
	Clay content	To determine sorption characteristics of soil.
	Moisture content	To determine conductivity of air through soil.
	<b>Chemical:</b> Organics	To determine concentration of target or interfering constituents, pretreatment needs, extraction medium.
	Metals (total)	To determine concentration of target or interfering constituents, pretreatment needs, extraction medium.
	Metals (leachable)	To determine mobility of target constituents, post-treatment needs.
	<b>Contaminant characteristics:</b> -Vapor pressure -Solubility -Henry's Law constant -Partition coefficient -Boiling point -Specific gravity	To aid in selection of extraction medium.
	Total organic carbon (TOC), humic acid	To determine presence of organic matter, sorption characteristics of soil.
	Cation exchange capacity (CEC)	To determine sorption characteristics of soil.
	pH Cyanides, sulfides, fluorides	To determine pretreatment needs, extraction medium. To determine potential for generating toxic fumes at low pH.
Chemical dehalogenation	<b>Physical:</b> Moisture content	To determine reagent requirements.
	<b>Chemical:</b> Aromatic halides	To determine concentration of target constituents, reagent requirements.
	Metals	To determine concentration of other alkaline-reactive constituents, reagent requirements.
	pH	To determine reagent requirements.
Oxidation/reduction	<b>Physical:</b> Total suspended solids	To determine the need for slurring to aid mixing.
	<b>Chemical:</b> Chemical oxygen demand (COD)	To determine the presence of oxidizable organic matter, reagent requirements.
	Metals (Cr <sup>+3</sup> , Hg, Pb, Ag)	To determine the presence of constituents that could be oxidized to more toxic or mobile forms.
	pH	To determine potential chemical interferences.

## Assessment of Problem

Assessment of the problem involves organizing the information obtained from site characterization activities to evaluate the transport and degradation behavior of each chemical of concern at a site under consideration. Specifically, the rate of transport can be compared with the rate of degradation to determine if transport is significant relative to degradation. This approach to problem(s) assessment will allow chemicals to be prioritized individually according to: 1) magnitude and rate of transport (escape) from a site; 2) persistence; and 3) pathway(s) of migration from a site. Treatment technique evaluation and selection can then be based upon specific combinations of chemical-physical phase-migration pathway(s).

Interfacing "soil and subsurface-based behavior characteristics" (Table II) of specific contaminants with specific site and subsurface properties allows an assessment of the problem(s) related to contamination of other media (due to mobility), including ground water under the contaminated area, atmosphere over the site or at the site boundaries, surface waters, etc., and/or persistence of chemicals at a site. Pathways of movement and potential mechanisms of removal of contaminants at a specific site are illustrated in Figure 2. This element of the methodology functions to identify chemicals that will: 1) migrate upward (volatilization); 2) migrate downward (leaching); 3) migrate laterally (aqueous plume and pure product); 4) degrade; and 5) remain at the site as persistent chemicals. By ranking the chemicals in the order in which they migrate or persist, chemicals can be prioritized with regard to urgency for treatment and for monitoring.

Site characteristics identified in Table II, including sorption, degradation, and volatilization at a site, can be determined in laboratory mass balance tests, using waste/soil mixtures from a site, to evaluate the fate of the waste at the site, and to generate specific data that can be used to develop treatment approaches. An example of a laboratory flask apparatus that can be used to develop a chemical mass balance by measuring interphase transfer potential of chemicals as well as degradation potential at a site is illustrated in Figure 3.

The contaminated material is placed in a flask, which is then closed and incubated under controlled conditions for a period of time. During the incubation period, air is drawn through the flask and then through a sorbent material. Volatilized materials are collected by the sorbent and are measured to provide an estimate of volatilization loss of the constituents of interest. At the end of the incubation period, a portion of the contaminated soil is treated with an extracting solution to determine the extent of loss of the constituents in the soil matrix. This loss can be attributed to degradation and possible immobilization in the soil materials. Selection of an appropriate extracting solution and procedure is necessary to maximize constituent recovery from a soil-waste mixture.<sup>81</sup> Another portion of the soil is leached with water to determine leaching potential of remaining constituents. Abiotic and biological processes involved in removal of the parent compound are evaluated by comparing microbially active soil/waste mixtures with mixtures that have been treated with a microbial poison, e.g., mercuric chloride or propylene oxide.

Samples generated from the different phases of the system in microcosm mass balance studies identified above can be analyzed for intermediate degradation products and used in bioassay studies to provide information concerning transformation and detoxification processes.

The use of a procedure incorporating features illustrated by the use of this microcosm is crucial in order to obtain a materials balance of waste constituents in the soil system. Examples of such protocols may be found in U.S. EPA guidance documents and research reports,<sup>34,41,42</sup> and Park et al.<sup>82</sup>

Contaminated materials can also be spiked with radiolabelled chemicals; tracking the fate of the chemicals as they move through the multiple phases of the soil system also provides a material mass balance.

The mass balance approach identified above usually represents optimum conditions with respect to mixing, contact of solid materials with waste constituents, and homogeneous conditions throughout the laboratory microcosm, and therefore does not incorporate site nonhomogeneity in the evaluation. This aspect needs to be defined during site characterization activities and evaluated with regard to potential effect on fate and behavior regarding migration and persistence at the site (problem assessment).

In addition to the laboratory tests described, bench-scale reactors, pilot scale reactors and/or field scale plots may be used to generate mass balance information for problem assessment. The set of experimental conditions, e.g., temperature, moisture, waste concentration, etc., under which the studies were conducted should be presented along with experimental results.

## Utility of Mathematical Models for Problem Assessment

Information from the performance of site characterization and experimental mass balance studies may be integrated with the use of comprehensive mathematical modeling to aid in problem assessment. In general, models are used to analyze the behavior of an environmental system under both current (or past) conditions and anticipated (or future) conditions.<sup>83</sup> A mathematical model provides a tool for integrating degradation and partitioning processes with site/soil- and waste-specific characterization for simulating the behavior of organic constituents in a contaminated soil and for predicting the pathways of migration through the contaminated area, and therefore pathways of exposure to humans and to the environment. DiGuilio and Suffet<sup>84</sup> and Weaver et al.<sup>85</sup> have presented guidance on the selection of appropriate subsurface (vadose) zone models for site-specific applications, focusing on recognition of limitations of process

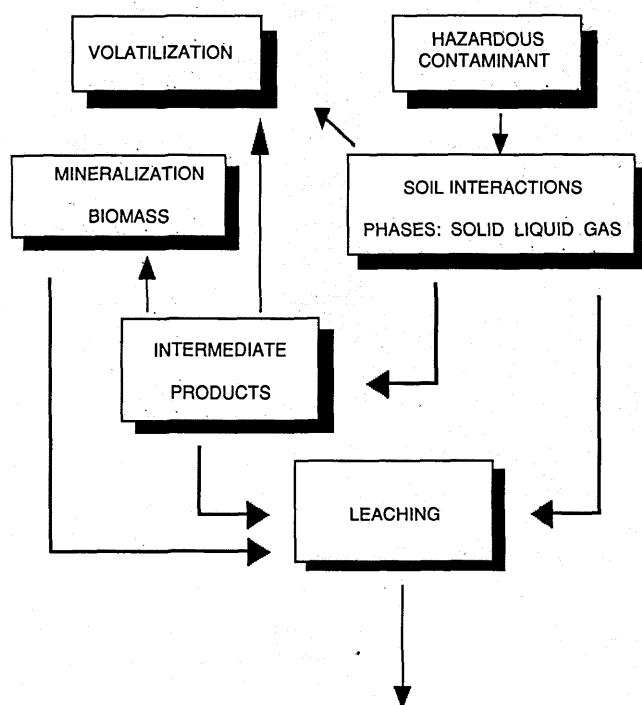


Figure 2. Fate of hazardous contaminants in soil.<sup>22</sup>

descriptions of models and difficulties in obtaining input parameters required by these process descriptions.

The Regulatory and Investigative Treatment Zone Model (RITZ Model), developed at the U.S. EPA Robert S. Kerr Environmental Research Laboratory by Short<sup>86</sup> is an example of a model that has been used to describe the potential fate and behavior of organic constituents in a contaminated soil system.<sup>87</sup> The Ritz Model is based on an approach developed by Jury.<sup>88</sup> An expanded version of RITZ, the Vadose Zone Interactive Processes (VIP) model incorporates predictive capabilities for the dynamic behavior of organic constituents in unsaturated soil systems under conditions of variable precipitation, temperature, and waste concentrations.<sup>34,89-92</sup> Both models simulate vadose zone processes, including volatilization, degradation, sorption/desorption, advection, and dispersion.<sup>93</sup>

For example, the VIP model was used to evaluate the relative tendencies for a group of pesticides to volatilize and to leach under specific waste-soil conditions.<sup>89</sup> Information that was input into the model included half-life (measured in laboratory tests), distribution coefficients ( $K_d$ ,  $K_h$ ,  $K_o$ ) (calculated), soil texture and moisture (measured), and site-specific climatic data (rainfall and temperature). Results are presented in Table IX. The ranking of pesticides provided by the model indicated that the tendency of the pesticides to volatilize was not similar to their tendency to leach (McLean

et al. 1988). This information can be used to assess the problem of which chemicals are likely to volatilize first, which to leach first, and which chemicals are persistent under site-specific conditions. Models can also be used to design studies for evaluation and selection of treatment options for these chemicals, as well as to design monitoring strategies (i.e., which chemicals to monitor in which media).

### Treatment Approaches

Information obtained from an integrated assessment (modeling) of the problem (migration and persistence), based upon a thorough characterization of waste/soil/site interactions, can be used to select treatment approaches for further evaluation with respect to technical and cost effectiveness factors. Results of characterization and assessment efforts can aid in the identification of constituents that will require treatment in the air (volatile) phase, in the leachate phase, and in the solid (soil) phase. This approach allows evaluation and comparison of different treatment systems identified previously (in situ, prepared bed, and in-tank). Specifically, if treatment is required, the information is used in order to: 1) determine containment requirements to prevent contamination of off-site receiver systems; 2) develop techniques to maximize mass transfer of chemicals affecting a process (e.g., affecting microorganism activity through ad-

**Table V.** Characterization parameters for immobilization techniques.<sup>80</sup>

Treatment technique	Parameter	Purpose and comments
Stabilization/ solidification (S/S)	<b>Physical:</b>	
	Description of materials	To determine waste handling methods (e.g., crusher, shredder, removal equipment).
	Particle size analysis	To determine surface area available for binder contact and leaching.
	Moisture content	To determine amount of water to add/remove in S/S mixing process.
	Density testing	To evaluate changes in density between untreated and treated waste.
	Strength testing	
	—Unconfined compressive strength	To evaluate changes in response to overburden stress between untreated and treated waste (e.g., material response to stress from cap).
	—Flexural strength	To evaluate material's ability to withstand loads over large area.
	—Cone index	To evaluate materials' stability and bearing capacity.
	Durability testing	To evaluate durability of treated wastes (freeze-thaw and wet-dry durability).
	<b>Chemical:</b>	
	pH	To evaluate changes in leaching as function of pH.
	Alkalinity	To evaluate changes in leaching as function of alkalinity.
	Interfering compounds	To evaluate viability of S/S process. (Interfering compounds are those that impede fixation reactions, cause adverse chemical reactions, generate excessive heat; interfering compounds varying with type of S/S).
Indicator compounds	To evaluate performance of S/S (i.e., leaching).	
Leach testing	To evaluate performance of S/S.	
Heat of hydration	To measure temperature changes during mixing.	
Vitrification	<b>Physical:</b>	
	Depth of contamination and water table	Technology is applied to unsaturated soils.
	Soil permeability	Dewatering of saturated soils may be possible. Technology is applied in unsaturated soils.
	Metal content of waste material and placement of metals within the waste	Greater than 5 to 15% by weight or significant amounts of metal near electrodes interfere with process.
	Combustible liquid/solid content of waste	Greater than 5 to 15% by weight interferes with process.
	Rubble content of waste Void volumes	Greater than 10 to 20% by weight interferes with process. Large, individual voids impede process.

**Table VI.** Characterization parameters for thermal treatment techniques.<sup>80</sup>

Treatment technique	Parameter	Purpose and comments
General	<b>Physical:</b>	
	Moisture content	Affects heating value and material handling.
	Ash content	To determine the amount of ash that must be disposed or treated further.
	Ash fusion temperature	High temperature can cause slagging problems with inorganic salts having low melting points.
	<b>Chemical</b>	
	Volatile organics, semivolatile organics	Allows determination of principal organic hazardous constituents (POHCs).
	POHCs	Allows determination of destruction removal efficiency (DRE).
	Total chlorine, fluorine	To determine air pollution control devices for control of acid gases.
	Total sulfur, total nitrogen	Emissions of SO <sub>x</sub> and NO <sub>x</sub> are regulated; to determine air pollution devices.
	Phosphorus	Organic phosphorus compounds may contribute to refractory attack and slagging problems.
Rotary kiln	<b>Physical:</b>	
	Particle-size distribution	Fine particle size results in high particulate loading in rotary kiln. Large particle size may present feeding problems.
	<b>Physical:</b>	
	Ash fusion temperature	For materials with a melting point less than 1600°F, particles melt and become sticky at high temperatures, which causes defluidization of the bed.
Fluidized-bed	Ash content	Ash contents greater than 65% can foul the bed.
	Bulk density	As density increases, particle size must be decreased for sufficient heat transfer.

dition of mineral nutrients, oxygen, additional energy sources, pH control products, etc., or removal of toxic products in order to enhance bioremediation); and 3) design a cost-effective and efficient monitoring program to evaluate effectiveness of treatment.

#### Containment Requirements

If the major pathway of transport is volatilization, containment and treatment with respect to volatilization control is required. An inflatable plastic dome erected over a contaminated site is a containment method that has been used to control escape of volatile constituents at hazardous waste sites.<sup>94</sup> Volatiles are drawn from the dome through a conduit and treated in an above ground treatment system. If leaching has been identified as important, control of soil water movement should be implemented. For example, if contaminated materials are expected to leach downward from the site, run-on and run-off controls can be implemented, or the contaminated materials can be temporarily removed from the site and a plastic or clay liner placed under the site.<sup>95-96</sup> When downward as well as upward migration are significant, both volatilization and leaching containment systems can be installed. Some hydrophobic chemicals do not tend to volatilize or to leach but are persistent within the soil solid phase; therefore containment efforts may not be required.

#### Maximizing Chemical Mass Transfer

An area of significant research concerns delivery and recovery technologies for maximizing mass transfer of chemi-

cals that affect the rate and/or extent of treatment. Murdoch et al.<sup>97</sup> discussed delivery and recovery technologies, many of which are derived from the petroleum and mining industries. While a liquid phase is usually employed for delivery of chemicals, some technologies utilize vapor and solid phases for delivery. Principal recovery technologies involve hydraulic, thermal, and chemical systems. Delivery and recovery techniques are important in influencing the success of technologies, including bioremediation, vapor extraction, and solidification/stabilization. Specific delivery and recovery systems for in situ treatment systems identified by the U.S. EPA include hydraulic fracturing, radial well drilling, ultrasonic methods, kerfing, jet-induced slurry method, carbon dioxide injection, hot brine injection, and cyclic pumping.<sup>3</sup>

#### Monitoring Program

A mass balance approach to monitoring can be performed at laboratory, pilot, and field scales. Monitoring efforts can be focused on the appropriate environmental phase to evaluate treatment effectiveness for specific chemicals. If a comprehensive and thorough evaluation of a specific contaminated system has been conducted, not all chemicals may need to be monitored in each phase. Specific chemicals will be associated with specific phases, which assists in the design of a monitoring plan that is chemical/phase specific. This approach also focuses analytical efforts so that methods development are chemical and phase specific.

Not only does the level of contamination associated with a particular treatment technology require monitoring, but also the system components, including delivery and recovery

systems, maintenance, and structures such as infiltration galleries, etc.

#### Utility of Mathematical Models for Technology Evaluation

A critical and cost-effective use of modeling in treatment (train) selection and evaluation is in the analysis of proposed or alternative future conditions, i.e., the model is used as a management or decision-making tool to help answer "what if" type questions.<sup>83</sup> Models may also be used to approximate and estimate the rates and extent of treatment that may be expected at the field scale under varying conditions.

Attempting to answer such questions through data collection programs would be expensive and practically impossible in many situations. For example, information can be generated to evaluate the effects of using differing approaches for enhancing microbial activity and for accelerating biodegradation and detoxification of the contaminated area by altering environmental conditions that affect microbial activity. Therefore, modeling may be used to assist in the design of treatability studies for considering and evaluating the application of different treatment technologies, and therefore assists in focusing resources (time and money).

**Table VII.** Characterization parameters for in situ treatment techniques.<sup>80</sup>

Treatment technique	Parameter	Purpose and comments
Vapor extraction —Vacuum extraction —Steam-enhanced  —Hot-air-enhanced	<b>Physical:</b> Vapor pressure of contaminants	To estimate ease of volatilization.
	Soil permeability, porosity, particle-size distribution	To determine if the soil matrix will allow adequate and fluid movement.
	Depth of contamination and water table	To determine relative distances; technology applicable in vadose zone.
Solidification/stabilization (undisturbed) —Pozzolanic —Polymerization —Precipitation	<b>Physical:</b> Presence of subsurface barriers (e.g., drums, large objects, debris, geologic formations)	To assess the feasibility of adequately delivering and mixing the S/S agents.
	Depth to first confining layer	To determine required depth of treatment.
Soil flushing —Steam/hot water —Surfactant —Solvent	<b>Physical:</b> Presence of subsurface barriers (e.g., drums, large objects, debris, geologic formations)	To assess the feasibility of adequately delivering the flushing solution.
	Hydraulic conductivity	To assess permeability of the soils.
	Moisture content (for vadose zone)	To calculate pore volume to determine rate of treatment.
	Soil/water partition coefficient	To assess removal efficiency and to correlate between field and theoretical calculations.
	Octanol/water partition coefficient	To assess removal efficiency and to correlate between field and theoretical calculations.
	CEC	To evaluate potential for contaminant flushing.
	Alkalinity of soil	To estimate the likelihood of precipitation.
Vitrification	<b>Chemical:</b> Major cation/anions present in soil	To estimate the likelihood of precipitation; to estimate potential for plugging of pore volumes.
	<b>Physical:</b> Depth of contamination and water table	Technology is only applied in the unsaturated zone.
Radio-frequency heating and direct-current heating	<b>Physical:</b> Depth of contamination and water table	Technology is only applied in the unsaturated zone.
	Presence of metal objects	Presence of metal objects precludes application.
Electrokinetics	<b>Physical:</b> Hydraulic conductivity	Technology applicable in zones of low hydraulic conductivity.
	Depth to water table	Technology applicable in saturated soils.
	<b>Chemical:</b> Presence of soluble metal contaminants	Technology applicable to soluble metals, but not organics and insoluble metals.
Microbial degradation —Aerobic —Anaerobic	<b>Physical:</b> Permeability of soil	To determine ability to deliver nutrients or oxygen to matrix and to allow movement of microbes.
	<b>Chemical/biological:</b> Contaminant concentration and toxicity	To determine viability of microbial population in the contaminated zone.

**Table VIII.** Examples of suggested site characterization activities, based on soils and subsurface materials as waste-receiver systems.<sup>7</sup>

Site	USEPA Region	Contaminants	Recommended site evaluation and characterization actions
Stamina Mills Superfund Site North Smithfield, RI	I	TCE	Determination of soil-water partition coefficients; investigation of soil physical and hydraulic properties; Simulation of contaminant transport
W. R. Grace & Co. Superfund Site Acton, MA	I	Acetone, benzene, & toluene	Selection of soil physical properties for fugacity modeling
Somersworth Landfill Somersworth, NH	I	Arsenic & organic compounds	Selection of leaching test suitable for high organic matter content soils to provide data for estimation of migration potential
Nascolite Superfund Site Millsville and Vineland, NJ	II	Methyl methacrylate (MMA)	Evaluation of residual soil concentrations during groundwater fluctuations; Development of appropriate extraction technologies based on chemical properties of MMA
Drake Chemical superfund Site Lock Haven, PA	III	Various wastes	Development of laboratory procedures: Determination of site-specific partition coefficients; Development of ContPro Model (revised version of Ritz Model)
Tyson's Dump	III	1,2,3-trichloro-propane, xylene, toluene, and ethyl-benzene	Determination of causes for plugging of SVE extraction wells with tarry materials
Anderson Development Co. Spill Cleanup Adrian, MI	V	4,4-methylene-bis-2-chloroaniline (MBOCA)	Recommendation of use of site-specific biotreatability study to determine feasibility of use of soil bioremediation
Montrose Chemical Site Los Angeles, CA	IX	DDT	Recommendations to design of laboratory soil biotreatment feasibility studies
Time Oil Site Tacoma, WA	X	PCE, PCA, & TCE	Development of soil-water and soil-air partitioning relationships for implementation of SVE
Frontier Hard Chrome Vancouver, WA	X	Chromium, lead, nickel, & cyanide	Development of estimates of leachate concentrations of contaminants at equilibrium between soil and water

### Treatability Studies

Treatability studies are used to provide specific information concerning the potential application of treatment technologies at field scale, by evaluating and comparing rate and extent of remediation among several technologies. Treatability studies can be conducted in laboratory microcosms or bench-scale reactors, pilot-scale facilities, or in the field. Laboratory treatability studies are generally screening studies used to establish the validity of a technology, to generate data that can be used as indicators of potential to meet performance goals, and to identify parameters for investigation during bench- or pilot-scale testing. Laboratory treatability studies are generally not appropriate for generating design or cost data.<sup>80</sup> Pilot-scale testing is conducted to generate information concerning quantitative performance, cost and design information. Three proposed categories of treatability testing and associated descriptions are included in Table X.<sup>80</sup>

Treatability study results are commonly used to provide information relating to rates and extent of treatment of hazardous organic constituents when mass transfer rates of potential limiting substances are not limiting the treatment. Treatability studies also usually represent optimum condi-

tions with respect to mixing, contact of soil solid materials with waste constituents and with microorganisms, and homogeneous conditions throughout the microcosm. Therefore, treatability studies provide information concerning potential levels of achievable treatment. Rate and extent of remediation in a prepared bed or in-situ system, and sometimes in in-tank reactors, are generally limited by accessibility and rate of mass transfer of chemical substances to the contaminated soil and removal of inhibitory microbial degradation products.<sup>61</sup>

Information from mass balance studies, including laboratory screening, bench- and pilot-scale studies, is combined with information concerning site and waste characteristics in order to determine applications and limitations of each technology. Information obtained from treatability studies should be focused on identifying ultimate limitations to the use of a remediation technology at a specific site, which usually are usually related to 1) time required for cleanup; 2) level of clean-up attainable; and 3) cost of clean-up.<sup>22</sup>

### Treatment Train Selection

The use of treatment trains is also important to consider in an engineering approach for using treatment techniques

for site remediation. For example, vacuum extraction is known to be applicable to unsaturated sites characterized by permeable materials containing volatile chemicals. Vacuum extraction can also be used for the removal of more semi-volatile chemicals by providing a source of oxygen (air) to subsurface microorganisms, where anoxic conditions exist due to relative slow replenishment of oxygen through atmospheric diffusion. This is an example of the use of one technology for the treatment of both volatile and semi-volatile chemicals in the subsurface.

Another example of the use of a treatment train for creosote contaminated soil and ground water involves: 1) product removal using a pumping system; 2) flushing with water and surfactants using pump and treat technology; and 3) in situ biodegradation of the residual contamination.<sup>98</sup> Each technology is employed in the order of ease of removal of creosote from the subsurface. The treatment train selected was based on a site characterization to identify where the creosote was located and the mass of creosote (including pure product) associated with subsurface phases, i.e., the vadose zone and aquifer materials. The problem assessment identified the following areas of concern: 1) potential offsite migration of pure product; 2) slow leaching of low levels of creosote contaminants sorbed to soil, subsurface, and aquifer materials; and 3) the presence of high molecular weight polycyclic aromatic compounds that are toxic to human health, are non-volatile, and have very low water solubilities. Each technology was evaluated in laboratory-scale treatability tests for treatment effectiveness and for ease of application to contaminated materials obtained from the site. Engineering design and implementation was based on results of site characterization, mass balance determinations at the site, and treatability studies.

Information from treatability studies is used to prepare an approach to the engineering design and implementation of a remediation system at a specific site that combines the mix of treatment techniques evaluated to construct a treatment train. The formulation of a treatment train for a site generally is based upon information from simulations (e.g., mathematical modeling) generated from mass balance studies, treatability studies, and site/soil characterization data.

#### Measurement and Interpretation of Treatment Effectiveness

Typically, soil samples are taken from a treatability reactor (in situ, prepared bed, or in-tank) from laboratory-, bench-, or pilot-scale studies, or from a field site, and extracted with a solvent or thermally desorbed. The concentration of compound is usually measured in the solvent extract of the soil or the thermal desorption stream using chemical instrumentation (e.g., gas or liquid chromatographs with appropriate detectors). This information is termed the "apparent loss" of a chemical and refers to the observation that the chemical disappears from the solvent or extraction phase, but does not necessarily represent a complete chemical mass balance.<sup>82</sup> The change in concentration of compound in the solvent with time is often used to calculate rate

**Table IX.** Ratios of concentration of pesticides between water/soil and air/soil at 15 cm after 81 days (ranked in order from greatest potential for leaching and volatilization to least potential).<sup>89</sup>

Pesticide	Leaching potential (concentration in soil water/ concentration in soil)	Pesticide	Volatilization potential (concentration in soil air/ concentration in soil)
Disulfoton	330	Toxaphene	7.4
Phorate	23	Disulfoton	$3.6 \times 10^{-2}$
Methylparathion	4.8	Phorate	$5.2 \times 10^{-3}$
Toxaphene	0.5	Heptachlor	$5.5 \times 10^{-3}$
Endosulfan	0.12	Endosulfan	$4.0 \times 10^{-4}$
Parathion	0.06	Aldrin	$2.0 \times 10^{-5}$
Heptachlor	0.06	Methylparathion	$1.2 \times 10^{-5}$
Aldrin	0.0009	Parathion	$1.6 \times 10^{-6}$

and extent of decrease in the concentration of compound in soil. This information is commonly used to interpret treatment effectiveness for different technologies and to determine engineering strategies and management approaches, including: 1) time required to attain cleanup target concentrations for a soil; and 2) effects of environmental factors or experimental variables (chemical, physical, or biological) on treatment effectiveness.

However, additional information is needed in order to accurately measure as well as interpret treatment effectiveness. In order to understand treatment mechanisms and to base the selection of treatment technologies on a rational approach, identification and measurement of distribution among the physical phases that comprise a soil system is necessary, as well as identification and differentiation of the mechanisms by which a compound may be chemically altered in a soil system.<sup>41,82,91,99-102</sup>

Enhancing information obtained concerning rate of apparent loss of chemicals from a soil extract with information concerning interphase transfer potential between solid and gas phases of soil as well as with knowledge of mechanisms of interactions of compounds with soil phases will provide the basis for a more rational approach to remediation of contaminated soil. Evaluation of remediation technology effectiveness can be based upon specific media (soil, air) and upon specific mechanisms, such as recovery of the air phase or enhancement of abiotic destruction or biological degradation, to improve treatment. Evaluation of interphase transfer also allows characterization of routes by which chemicals may migrate from the soil to the multimedia environment that lead to human exposure. Thus, this method for measuring treatment effectiveness is also valuable in the determination of risk reduction and implementation of risk management strategies.<sup>82</sup>

**Table X.** General comparison of laboratory screening, bench-scale testing, and pilot-scale testing.<sup>80</sup>

Tier	Type of data generated	Critical parameters	No. of replicates	Study size	Usual process type	Waste stream volume	Time required	Cost, \$
Laboratory screening	Qualitative	Several	Single/duplicate	Jar tests or beaker studies	Batch	Small	Hours/day	10,000-50,000
Bench-scale testing	Quantitative	Few	Duplicate/triplicate	Bench-top (some larger)	Batch or continuous	Medium	Days/week	50,000-250,000
Pilot-scale testing	Quantitative	Few	Triplicate or more	Pilot-plant (onsite or offsite)	Batch or continuous	Large	Weeks/month	250,000-1,000,000

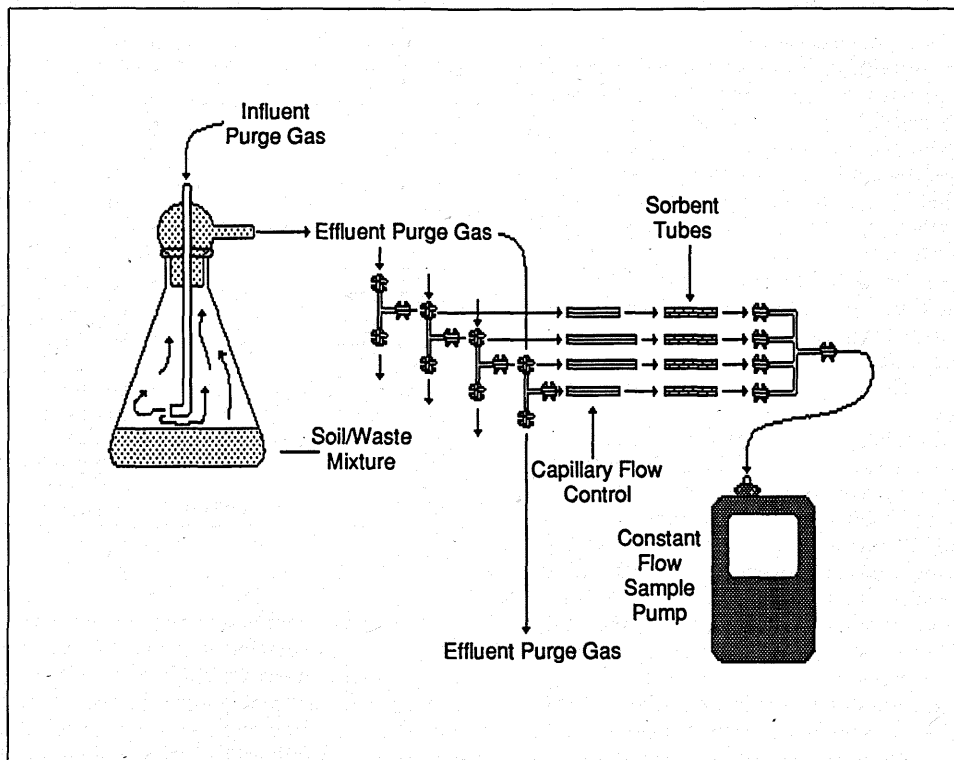


Figure 3. Laboratory flask apparatus used for mass balance measurements.<sup>22</sup>

The laboratory flask apparatus used for mass balance determinations (Figure 3) can also be used to measure and compare potential effectiveness for different treatment scenarios.

## Remediation Techniques for Contaminated Soils

### Overview

At the present time, many remedial techniques are being used and evaluated for use in the clean-up of contaminated soils. Participants in the U.S. EPA SITE program that are testing technologies applicable to contaminated soils are listed in Tables XI and XII.<sup>30</sup> Technologies applicable to contaminated soils currently being demonstrated and evaluated in the NATO/CCMS Pilot Study on "Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater" are summarized in Table XIII.

Selected physical, chemical, biological, thermal, and fixation/encapsulation soil remediation techniques were categorized as in situ, prepared bed, and/or in-tank reactors and are summarized in Table XIV. Each soil remediation technique was also evaluated with respect to function (separation, detoxification, etc.), potential for formation of residuals/transformation products, applications, and limitations. A subset of these techniques, evaluated at pilot- or field-scale, was selected for additional description.

### In Situ Techniques

#### Soil Vacuum Extraction (SVE)

**Process description:** Referred to as soil vapor extraction (SVE), forced air venting, or in situ air stripping, this tech-

nique involves extraction of air from unsaturated soil. Clean air is injected or passively flows into the unsaturated zone where volatile chemicals partition from soil water into soil air, with relative partitioning based on the air/water partition coefficient ( $K_h$ ) or Henry's Law constant.<sup>5</sup>

**Components and operation:** Typically, components of SVE consist of vacuum extraction wells (Figure 4), air inlet wells, and vapor monitoring wells distributed across a contaminated site, and a blower(s) to control air flow. Extraction wells may be placed vertically or horizontally across a site. Vertical alignment is typical for deeper contamination zones and for residues in radial flow patterns.<sup>103</sup>

**System variables:** Important system variables affecting the performance of SVE include properties of the chemical (vapor pressure and volatilization) and properties of the site (soil moisture content, soil texture, distribution of contaminants). Where chemicals exist in pure form, vapor pressure of the chemical is important, with vapor pressures above 14 mm Hg at 20° C desirable for application of SVE. When chemicals are distributed in the water phase in the soil, Henry's Law constant is important, with dimensionless Henry's constant above 0.01 (mg/L/mg/L) desirable for use of SVE.<sup>5</sup> Since movement of volatile organic chemicals (VOCs) is generally 10,000 times faster in a gas phase than in a water phase, VOC removal is expected to be enhanced by decreasing soil moisture. However, when soil is very dry, which may occur when dry air is drawn through soil, VOCs may adsorb directly onto mineral surfaces, where the magnitude of sorption is increased and consequently volatilization is decreased (Figure 5). Henry's Law constant is not appropriate under these conditions, since partitioning is between air and soil phases only. When moisture is added to soil, the effect is reversible. The moisture content at which a decrease in vapor density becomes apparent is often termed the criti-



cal moisture content and is generally defined as being equivalent to approximately a monolayer of water molecules coating the soil particles.<sup>104,105</sup> Johnson and Sterrett<sup>106</sup> noted that dichloropropane concentrations were correlated with ambient air moisture during the use of SVE at a site in Benson, Arizona.

If contaminated soil contains immiscible fluids in the form of oils, petroleum hydrocarbons, etc., the four-phase system discussed previously is operative. In this system, chemical volatility will be affected by the chemical vapor pressure and mole fraction within the immiscible oil fluid, and governed by Raoult's Law:

$$P_a = X_a P_a^o \quad (17)$$

where  $P_a$  = vapor pressure of solvent over solution (mm Hg),  $X_a$  = mole fraction of solvent in solution, and  $P_a^o$  = vapor pressure of pure solvent (mm Hg).

For contamination by hydrocarbons with multiple components, volatilization will proceed such that lower molecular weight chemicals will preferentially volatilize compared to higher molecular weight compounds. Through this process of weathering of the waste-soil mixture, SVE extraction efficiency is observed to decrease to less than 10 percent when the fraction of gasoline remaining is approximately 40 per-

cent.<sup>107</sup> Therefore, measurement of general parameters such as total hydrocarbons is not sufficient to indicate the removal efficiency of individual constituents.

Soil texture has been evaluated as it influences air permeability.<sup>108</sup> In less permeable media, such as glacial till and clayey soils, secondary permeability or porosity (fractures) will dominate air flow. The results will be rapid removal of VOCs in fractures and slow removal in the soil matrix. Pneumatic pump tests in the field are recommended for site-specific evaluation of the application of SVE.

Due to release of VOCs from the soil matrix when extraction wells are temporarily turned off, concentrations of VOC increase in soil air (referred to as "VOC rebound effect"), with an equilibrium concentration determined by Henry's Law constant. When blowers are turned on, an increase in the concentration of extracted vapor from the soil will be observed. Diffusive release from subsurface stratigraphy of less permeability will cause the slow continual release of chemicals into the soil gas phase (Figure 6).<sup>5</sup>

*Design:* Design considerations affecting SVE include extraction well spacing and extraction well depth. As permeability decreases, well spacing decreases, with typical well spacings of 10 m to 30 m common. Also, air circulation generally is not significant below the screened interval for extraction wells.

**Table XI.** SITE demonstration program participants with technologies applicable to remediation of contaminated soils.<sup>30</sup>

Developer	Technology	Applicable waste <sup>a</sup>	
		Inorganic	Organic
American Combustion Technologies, Inc. Norcross, GA	Pyreton oxygen burner	NA	Non-specific
American Toxic Disposal, Inc. Waukegan, IL	Vapor extraction system	Volatile	Volatile and semivolatile organics including PCBs, PAHs, PCPs, some pesticides
AWD Technologies, Inc. Burbank, CA	Integrated vapor extraction and steam vacuum stripping	NA	Volatile organic compounds
Biotrol, Inc. Chaska, MN	Soil washing system	Metals	High molecular weight organics
CF Systems Corporation Waltham, MA	Solvent extraction	NA	PCBs, volatile, and semivolatile organic compounds, petroleum byproducts
Chemfix Technologies, Inc. Metairie, LA	Solidification/stabilization	Heavy metals	High molecular weight organics
Chemical Waste Management, Inc. Oakbrook, IL	X*TRAX™ low temperature thermal desorption	NA	Volatile and semivolatile organics, PCBs
Dehydro-Tech Corporation East Hanover, NJ	Carver-Greenfield process for extraction of oily waste	NA	PCBs, dioxin, oil-soluble organics
Ecova Corporation Redmond, WA	In situ biological treatment	NA	Chlorinated solvents, non-chlorinated organic compounds
EPOC Water, Inc. Fresno, CA	Leaching and microfiltration	Specific for heavy metals	NA
Exxon Chemicals, Inc./Rio Linda Chemical Co. Long Beach, CA	Chemical oxidation/cyanide destruction	Cyanide	NA
GeoSafe Corporation Kirkland, WA	In situ vitrification	Non-specific	Non-specific
HAZCON, Inc. Brookshire, TX	Solidification/stabilization	Heavy metals	Not an inhibitor
Horsehead Resources Development Co., Inc. Monaca, Pa	Flame (slagging) reactor	Heavy metals	NA

<sup>a</sup> NA = non applicable

(Continued on next page)

**Table XI.** SITE demonstration program participants with technologies applicable to remediation of contaminated soils (continued).<sup>30</sup>

Developer	Technology	Applicable waste <sup>a</sup>	
		Inorganic	Organic
International Waste Technologies/ Geo-Con, Inc. Wichita, KS	In situ solidification/ stabilization	Non-specific	PCBs, other non-specific organic compounds
MoTec, Inc. Austin, TX	Liquid/solid contact digestion	NA	Halogenated and non- halogenated organic compounds, pesticides
Ogden Environmental Services San Diego, CA	Circulating fluidized bed combustor	NA	Halogenated and non- halogenated organic compounds
Ozonics Recycling Corp. Boca Raton, FL	Soil washing, catalytic/ ozone oxidation	Cyanide	Semivolatiles, pesticides, PCBs, PCP, dioxin
Resources Conservation Co. Bellevue, WA	Solvent extraction (BEST)	NA	Specific for high molecular weight organics
Retech, Inc. Ukiah, CA	Plasma reactor	Metals	Non-specific
S. M. W. Seiko, Inc. Redwood City, CA	In situ solidification/ stabilization	Metals	Semivolatile organic compounds
Shirco Infrared Systems, Inc.	Infrared thermal destruction	NA	Non-specific
Silicate Technology Corp. Scottsdale, AZ	Solidification/stabilization with silicate compounds	Metals, cyanide, ammonia	High molecular weight organics
Soliditech, Inc. Houston, TX	Solidification/stabilization	Metals	Non-specific
Solvent Services, Inc. San Jose, CA	Steam injection and vacuum extraction (SIVE)	NA	Volatile and semivolatile organic compounds
Terra Vac, Inc. San Juan, PR	In situ vacuum extraction	NA	Volatile and semivolatile organic compounds
Toxic Treatments (USA) Inc. San Francisco, CA	In situ steam/air stripping	NA	Volatile organic compounds and hydrocarbons
Wastech, Inc. Oak Ridge, TN	Solidification/stabilization	Non-specific, radioactive	Non-specific

<sup>a</sup> NA = non applicable

Where contamination is deep and permeability is high throughout the soil profile, the slotted (screened) interval should be extended to the maximum depth possible to maximize treatment, rather than slotted fully vertically.<sup>5</sup>

*Special application:* A promising aspect of SVE is potential application for the enhancement of biodegradation of volatile and semi-volatile chemicals in soils. SVE provides air to the vadose zone, and thus carries oxygen that can be used as the terminal electron acceptor by soil microorganisms to biodegrade chemicals. Air has a much greater potential than water for delivering oxygen to soil on a weight-to-weight basis and volume-to-volume basis. Oxygen provided by air is more easily delivered since the fluid is less viscous than water; higher oxygen concentration in air also provides a large driving force for diffusion of oxygen into less permeable areas within a soil formation.<sup>109</sup>

Hinchee<sup>110</sup> and Hinchee and Downey<sup>111</sup> successfully applied SVE for the enhancement of biodegradation of petroleum hydrocarbons in JP-4 jet fuel at Hill Air Force Base, Ogden, Utah, by increasing subsurface oxygen concentrations. Soil moisture was found to be a sensitive variable affecting biodegradation, with increased soil moisture (from 20 percent to 75 percent field capacity) related to increased biodegradation (Figure 7). Monitoring carbon dioxide and oxygen concentrations, as well as estimating the mass of VOC biodegraded, is recommended for evaluation of potential enhanced biodegradation.

In situ vacuum extraction has been demonstrated in Massachusetts as part of the Superfund SITE program,<sup>30,112</sup> in Michigan and Puerto Rico,<sup>113</sup> and at several other locations in the United States.<sup>3</sup>

#### Bioremediation

Wilson<sup>114</sup> identified biological processes, including microbial degradation, as an important mechanism for attenuating contaminants during transport through the vadose zone to the groundwater. In situ soil remedial measures using biological processes can reduce or eliminate continuing or potential groundwater contamination, thus reducing the need for extensive groundwater monitoring and treatment requirements.<sup>114-116</sup> In situ biological remediation of soils contaminated with organic chemicals is also an alternative treatment technology for achieving a permanent clean-up remedy at hazardous waste sites, as encouraged by the U.S. EPA for implementation of the Superfund Amendments and Reauthorization Act (SARA) of 1986.

*Process description:* In situ bioremediation involves the use of naturally occurring microorganisms to degrade and/or detoxify hazardous constituents in the soil at a contaminated site to protect public health and the environment. Bioremediation techniques for contaminated soils have been addressed at several recent scientific meetings and conferences.<sup>21,118-121</sup> The use of bioremediation techniques in

**Table XII.** SITE emerging technology program participants with technologies applicable to remediation of contaminated soils.<sup>30</sup>

Developer	Technology	Applicable waste <sup>a</sup>	
		Inorganic	Organic
Babcock & Wilcox Co. Alliance, OH	Cyclone combustor	Non-specific	Non-specific
Battelle Memorial Institute, Columbus Division Columbus, OH	In situ electroacoustic decontamination	Specific for heavy metals	NA
Enviro-Sciences, Inc. Randolph, NJ	Low energy solvent extraction	NA	PCBs, other non-specific organic compounds
Harmon Environmental Services, Inc. (formerly Envirite Field Services, Inc.) Auburn, AL	Soil washing	NA	Heavy organic compounds
IT Corporation Knoxville, TN	Batch steam distillation/ metal extraction	Non-specific	Non-specific
Western Research Institute Laramie, WY	Contained recovery of oily wastes (CROW)	NA	Coal tar derivatives, petroleum byproducts

<sup>a</sup> NA = non applicable

conjunction with chemical and physical treatment processes, i.e., the use of a "treatment train," is an effective means for comprehensive site-specific remediation.<sup>96</sup>

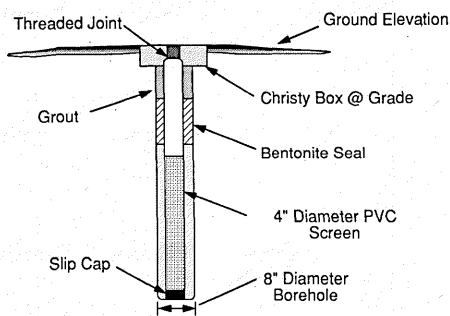
Four approaches are generally used for in situ biological treatment, including: 1) enhancement of biochemical mechanisms for detoxifying or degrading chemicals; 2) augmentation with exogenous acclimated or specialized microorgan-

*System variables:* Microbial ecologists have identified ranges of critical environmental conditions that affect aerobic activity of soil microorganisms (Table XV). Many of these conditions are controllable and can be modified to enhance activity.<sup>24,54,59,122</sup>

*System design:* Information for design of in situ bioremediation for treatment of hazardous waste-contaminated soil is based on land treatment.<sup>33-34,123</sup> Modification of land treatment designs provide a significant information base for designing in situ soil remediation systems.

*Special application:* The application of cooxidation processes for the biodegradation of high molecular weight polycyclic aromatic hydrocarbons (PAHs) present in oil (NAPL) phases in soil has been investigated by Keck et al.<sup>58</sup> In certain cases, PAH degradation may be limited by the rate of primary substrate (oil) degradation, which is limited by the rate of supply of electron acceptor (oxygen) to the subsurface. In the study by Keck et al., aerobic conditions were not sufficient to stimulate biodegradation of high molecular weight PAHs; however, when PAHs were present in an oily matrix in the soil, and the soil was tilled to supply oxygen, PAHs were observed to exhibit faster degradation kinetics.

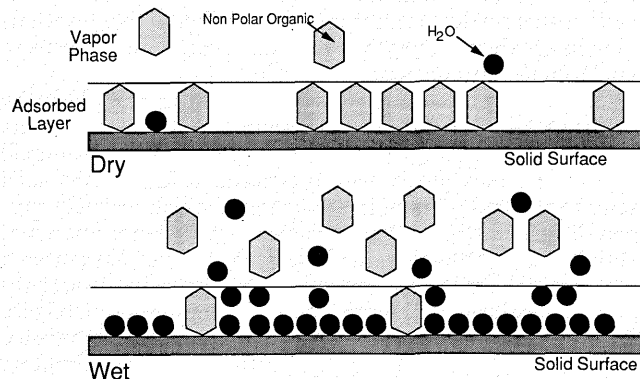
There is also increasing evidence that some halogenated compounds may be degraded under methanogenic conditions through a process of reductive dehalogenation.<sup>124-126</sup> Kobayashi and Rittmann<sup>127</sup> determined that the redox po-



**Figure 4.** Schematic of a gas extraction well.<sup>5</sup>

isms; 3) application of cell-free enzymes; and 4) vegetative uptake.<sup>3</sup> Enhancement of biochemical mechanisms may involve: 1) control of soil factors such as moisture, pH, nutrients, and temperature to optimize microbial activity; 2) addition of organic amendments to stimulate cooxidation or cometabolism; 3) control of soil oxygen by moisture control to accomplish aerobic or anaerobic biodegradation; and 4) addition of colloidal gas aphrons (microscopic bubbles of gas) to increase the concentration of terminal electron acceptor (oxygen) in the soil and thereby enhance aerobic biodegradation.<sup>3,5,21,58</sup>

*Components and operations:* Components generally include: 1) delivery systems, such as injection nozzles, plows, and irrigation systems, to accomplish the delivery of water, nutrients, oxygen, organic matter, specialized microorganisms, and/or other amendments, as required; and 2) run-off and run-off controls for moisture control and waste containment.<sup>3,23</sup>



**Figure 5.** Effect of moisture on VOC adsorption and desorption in soil—VOC adsorption with two moisture regimes.<sup>5</sup>

**Table XIII.** NATO/CCMS projects for the remediation of contaminated soils.<sup>10</sup>

Treatment Organization/site	Treatable contaminants					Specific contaminants treated	Treatment location	Status of technology
	Aliphatic hydrocarbons	Aromatic hydrocarbons	Halogenated hydrocarbons	Heavy metals	Petroleum fuels, oil			
<b>Biological</b>								
Enhanced aerobic restoration U.S. Air Force, Battelle; Eglin Air Force Base, FL, United States	✓	✓			✓	Jet fuel	In-situ	Experimental
Microbial treatment Former gas works, Fredensborg, Denmark		✓		✓		Polycyclic aromatic hydrocarbons, phenols, cyanides	On-site, in-situ	Demonstration
<b>Chemical/Physical</b>								
K-PEG process U.S. Environmental Protection Agency, Wide Beach, NY, United States	✓	✓	✓	✓	✓	PCBs, dioxin	On-site, mobile	Demonstrated
High pressure soil washing Scrap metal & copper refinery, Berlin, Federal Republic of Germany		✓	✓	✓	✓	Lead, PAHCs	On-site, mobile	Commercial
High pressure soil washing and oxidation Goldbeck Haus, Hamburg, Federal Republic of Germany		✓				Phenol, kresol	In-situ	Demonstration
Soil vapor extraction U.S. Environmental Protection Agency, Verona Well Field Battle Creek, MI, United States		✓	✓	✓	✓	Halogenated and aromatic hydro- carbons	In-situ	Demonstrated
<b>Stabilization/Solidification</b>								
In-situ vitrification Parsons Chemical Site, Michigan, United States	✓	✓	✓	✓		Mercury	In-situ	Experimental
<b>Electrokinetic</b>								
Electro-reclamation Loppersum, The Netherlands				✓		Arsenic	In-situ	Commercial
<b>Thermal</b>								
Thermal desorption and destruction (radiation heating) Dekonta GmbH, Hamburg, Federal Republic of Germany		✓	✓			Chlorobenzenes, Chlorophenols, Hexachlorocyclo- hexane, dioxins, furans	On-site	Experimental

tential of the environment must be below 0.35 V for significant reductive dechlorination to occur. Reductive reactions may be catalyzed by both abiotic and biochemical means in anaerobic environments.

Oxygen may be consumed faster than it can be replaced by diffusion from the atmosphere, and the soil may become anaerobic. Clay content of soil and the presence of organic matter also may affect oxygen content in soil. Clayey soils tend to retain a high moisture content, which restricts oxygen diffusion, while organic matter may increase microbial activity and deplete available oxygen. Loss of oxygen as a metabolic electron acceptor induces a change in the activity and composition of the soil microbial population. Obligate anaerobic organisms and facultative anaerobic organisms, which use oxygen when it is present or switch to alternative electron acceptors such as nitrate or sulfate in the absence of oxygen, become the dominant populations. Additional information concerning in situ anaerobic bioremediation can be

found in the document, "Handbook on In Situ Treatment of Hazardous Waste-contaminated Soils."<sup>3</sup>

In contrast to the possibility of vegetative accumulation of chemicals for harvesting and removal from a site, the use of plants for stimulating microbial activity in soil that results in increased biodegradation of target organic chemicals is currently being investigated by Walton<sup>128</sup> and Aprill and Sims.<sup>129</sup> In soils with low levels of contamination, plant roots may stimulate cooxidation or cometabolism of target co-substrates by providing exudates that serve as carbon and energy substrates for soil microorganisms.

The environmental factors presented in Table XV, as well as waste and other soil/site characteristics, interact to affect microbial activity at a specific contaminated site. Computer modeling techniques are useful design and evaluation tools to describe interactions and their effects on bioremediation treatment techniques for organic constituents in a specific situation.

### Contaminant Immobilization

**System description:** In situ immobilization describes the relative tendency of a contaminated soil to retain hazardous chemicals in the solid phase, thereby preventing interphase transfer into aqueous, gaseous, and/or other mobile (fluid) phases in the soil environment. Immobilization techniques include a broad range of alternatives that function to reduce the rate of release of contaminants from the soil so that concentrations along exposure pathways are held within acceptable limits. Primary natural immobilization mechanisms in soil are sorption, ion exchange, and precipitation. These techniques are based on soil processes that have been previously discussed in this paper and are presented in detail in Sims et al.<sup>23-24</sup>

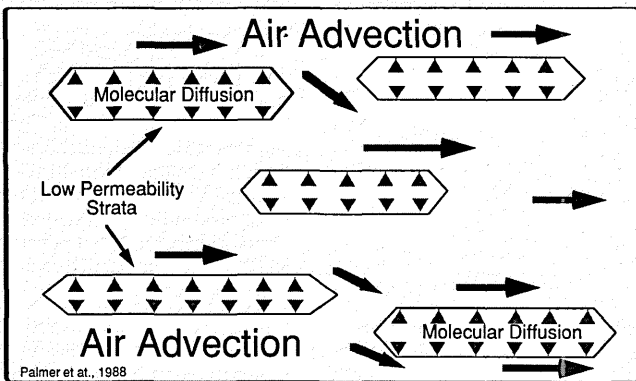


Figure 6. Diffusive release of contaminants from the soil phase into the gas phase.<sup>5</sup>

Solidification and stabilization represent immobilization techniques designed to accomplish one or more of the following: 1) produce a solid from a liquid or semi-solid waste; 2) reduce contaminant solubility; and/or 3) decrease the exposed surface area across which transfer may occur. Solidification may involve encapsulation of fine waste particles (mi-

croencapsulation) or large blocks of waste (macroencapsulation). Stabilization refers to the process of reducing the hazardous potential of waste material by converting the contaminants into their least soluble, mobile, or toxic form.<sup>3</sup> A milestone publication providing additional details on this technique is the "Handbook for Stabilization/Solidification of Hazardous Wastes."<sup>130</sup>

**System components and operation:** Delivery systems for reagents to the contaminated area include: 1) injection systems; 2) soil surface applicators; and/or 3) delivery and application of electrical energy for melting soils and rocks that contain hazardous materials. Equipment required for preparing, mixing, and applying reagents depends upon the reagent, process, and depth of contamination.<sup>3</sup>

**System variables:** Important parameters identified by Truett et al.<sup>131</sup> include reagent viscosity, permeability of soils, porosity of waste materials and soil, distribution of waste in surrounding material (rocks, soils, etc.), and rate of reaction. The most significant challenge in applying solidification/stabilization treatment in situ is achieving uniform mixing of the chemical agent added with the contaminated soils.<sup>3</sup>

**Design:** Design factors involve delivery and mixing system to obtain complete and uniform distribution of added reagent throughout the contaminated soil.<sup>3</sup>

**Special application:** This technique was applied and evaluated under the Superfund SITE program for treatment of polychlorinated biphenyl (PCB) contaminated soils.<sup>132</sup> Eight additional application sites were summarized by the U.S. EPA.<sup>3</sup>

### Contaminant Mobilization

**System description:** Mobilization of organic and/or inorganic contaminants from soil may be accomplished using soil flushing, with recovery and treatment of the elutriate.<sup>3,23</sup> Flushing solutions generally include water, acidic and basic solutions, surfactants, and solvents. The solutions function to partition a contaminant into the liquid phase through volume of added liquid or through decreasing the distribution coefficient between the soil and the flushing phase.<sup>24,133</sup>

**System components and operation:** Components consist of the flushing solution and delivery and recovery systems,

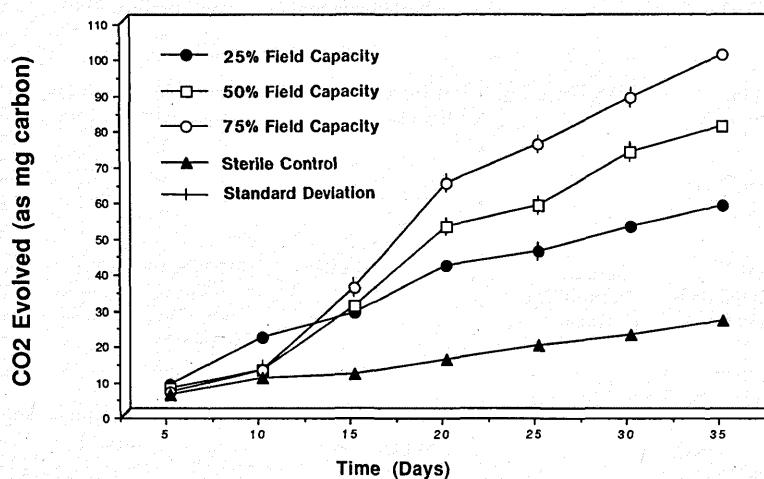


Figure 7. Enhancement of bioremediation of gasoline components using vacuum extraction of soil amended with nutrients and moisture.<sup>110-111</sup>

**Table XIV.** Selected remediation techniques possibly suitable for clean-up of contaminated soils.<sup>25-26,28-29</sup>

Remediation Techniques Type of treatment technology	Treatment category	Function	Possible residuals/transformation products	Possible applications	Possible limitations
<b>Physical/chemical treatment</b>					
Low Temperature Thermal Stripping (including radio frequency heating)	In-tank; In situ	Separation	Off-gas; Spent carbon or ash from afterburner; Processed soil; Hazardous emissions from in situ applications	Compounds of low water solubility and high volatility	Limited to organics with Henry's Law constant greater than $3.0 \times 10^{-3}$ atm-m <sup>-3</sup> /mole and boiling points less than 800°; More effective for soils with low contents of organic matter and moisture
Soil Washing	In-tank	Separation; Volume Reduction	Extracted materials; Water/flushing agent mix	Organics and inorganics; Most suitable for soils contaminated with only a few specific chemicals	Unfavorable contaminant separation coefficients; Less effective with complex mixtures of waste types and variation in waste composition; Unfavorable soil characteristics include: high humic content, soil/solvent reactions, high silt and clay content, and clay soils containing semivolatiles; Unfavorable washing fluid characteristics include: difficult recovery of solvent or surfactant, poor treatability of washing fluid, reduction of soil permeability, and high toxicity of washing fluid
Soil Flushing	In situ	Separation; Volume Reduction	Extracted materials; Water/washing agent mix	Organics and inorganics; Most suitable for soils contaminated with only a few specific chemicals	Unfavorable contaminant separation coefficients; Less effective with complex mixtures of waste types and variation in waste composition; Unfavorable soil characteristics include: variable soil conditions, high organic matter content, soil/solvent reactions, high silt and clay content, and clay soils containing semivolatiles; Unfavorable flushing fluid characteristics include: difficult recovery of solvent or surfactant, poor treatability of washing fluid, reduction of soil permeability, and high toxicity of washing fluid; Requires containment of leachate and ground water to prevent off-site groundwater contamination
Soil Vacuum Extraction (SVE)	In situ; Prepared bed	Separation	Volatile organics and volatile toxic metals	Volatile organics and toxic metals; May be enhanced by the use of steam	Soil heterogeneity (e.g., permeability, texture); Not applicable to saturated materials or miscible compounds
Glycolate Dechlorination	In-tank; In situ	Detoxification	Water/reagent mix; Reaction products	Dehalogenation of aromatic halide compounds	Heat and excess reagent required for soils with greater than 20% moisture and contaminant concentrations greater than 5%, and that contain competing reactive metals (e.g., aluminum)
Neutralization	In situ; Prepared bed; In-tank	Detoxification; Immobilization	Precipitated salts	Waste acids and alkalis to reduce reactivity and corrosiveness	Compatibility of waste and treatment chemical to prevent formation of more toxic or hazardous compounds
<b>Physical/chemical treatment</b>					
Oxidation	In situ; Prepared bed; In-tank	Detoxification	Oxidized reaction products	Cyanides and oxidizable organics	Possible explosive reactions; Production of more toxic or hazardous products; Non-selective

**Table XIV.** Selected remediation techniques possibly suitable for clean-up of contaminated soils (continued).<sup>25-26,28-29</sup>

Remediation Techniques Type of treatment technology	Treatment category	Function	Possible residuals/transformation products	Possible applications	Possible limitations
Photolysis	Prepared bed;	Detoxification	Reaction products	Dioxins; Nitrated wastes	Inability of light to penetrate soil.
Precipitation	In situ; Prepared bed; In-tank	Separation; Volume Reduction; Immobilization	Precipitated metals	Metals; Certain anions;	Unfavorable effects on soil permeability; Long-term stability unknown
Reduction	In situ; Prepared bed; In-tank	Detoxification	Reduced reaction products	Chromium, silver, and mercury	Possible explosive reactions; Production of more toxic or hazardous products; Non-selective
Carbon Adsorption	In situ; Prepared bed	Separation; Immobilization	Processed soil	Organic wastes; Wastes with high molecular weight and boiling point and low solubility and polarity;	Long-term stability unknown;
Ion Exchange	In situ; Prepared bed	Separation; Immobilization	Processed soil	Metal contaminants	Selectivity/competition limitations; pH requirements
<b>Thermal Treatment</b> Fluidized Bed	In-tank	Volume Reduction; Detoxification	Off-gases (possibly acidic and with incomplete combustion products); Treated materials with residual metals; Fly ash; Scrubber water	Halogenated and nonhalogenated organics; Inorganic cyanides	High maintenance requirements; Waste size and homogeneity requirements; Applicable to wastes with low sodium and metal contents
Infrared	In-tank	Volume Reduction; Detoxification	Off-gases (possibly acidic and with incomplete combustion products); Treated materials with residual metals; Fly ash; Scrubber water	Halogenated and nonhalogenated organics; Inorganic cyanides	Limited particle sizes, so may require size reduction equipment
Pyrolysis	In-tank	Volume Reduction; Detoxification	Nonvolatile char and ash (metals, salts, and particulates)	Wastes not conducive to conventional incineration; Wastes with volatile metals or recoverable residues	Small capacity
Rotary Kiln	In-tank	Volume Reduction; Detoxification	Off-gases (possibly acidic and with incomplete combustion products); Treated materials with residual metals; Fly ash; Scrubber water	Halogenated and nonhalogenated organics; Inorganic cyanides	High particulate emissions; Limited particle sizes, so may require size reduction equipment
<b>Biological treatment</b> Aerobic Bioremediation	In-tank Prepared bed; In situ	Detoxification	Hazardous volatile emissions; Incomplete and possibly hazardous degradation products; Leachates in soil systems	Biodegradable organic wastes	Ability to control environmental factors conducive to biodegradation; Formation of more toxic or hazardous transformation products; Prepared bed: areal limitations due to cost of bed preparation;
Anaerobic Bioremediation	In-tank Prepared bed; In situ	Detoxification	Hazardous volatile emissions; Carbon dioxide, methane and other gases; Incomplete and possibly hazardous degradation products; Leachates in soil systems	Certain halogenated organics	May require long treatment periods; Incomplete treatment, possibly requiring aerobic conditions to complete degradation process

**Table XIV.** Selected remediation techniques possibly suitable for clean-up of contaminated soils (continued).<sup>25-26,28-29</sup>

Remediation Techniques Type of treatment technology	Treatment category	Function	Possible residuals/transformation products	Possible applications	Possible limitations
Biological Seeding	In-tank Prepared bed; In situ	Detoxification	Hazardous volatile emissions; Incomplete and possibly hazardous degradation products; Leachates in soil systems	Many biodegradable organic wastes	Survival and activity of organisms in introduced environment (affected by environmental factors and competition with native species)
Composting	In-tank Prepared bed	Detoxification	Hazardous volatile emissions; Incomplete and possibly hazardous degradation products; Leachates in soil systems	Biodegradable organic wastes	Maintenance of optimum environmental conditions for biological activity; Requires large amounts of compost materials mixed with only about 10% wastes
Enzyme Addition	In-tank Prepared bed; In situ	Detoxification	Hazardous volatile emissions; Incomplete and possibly hazardous degradation products; Leachates in soil systems	Certain biodegradable organic wastes	Activity and stability of introduced enzymes in natural systems
<b>Fixation/encapsulation</b> Cement Solidification	In-tank; In situ	Storage; Immobilization	Leachates; Hazardous volatile emissions; solidified waste materials	Metal cations; Latex and solid plastic wastes	Incompatible with large amounts of dissolved sulfate salt or metallic anions such as arsenates or borates; Setting time increased by presence of organic matter, lignite, silt, or clay; Requires complete and uniform mixing of soils and reagents; Long-term stability unknown; May reduce soil permeability and increase run-off
Glassification/ Vitrification	In-tank; In situ	Storage; Immobilization	Leachates; Hazardous volatile emissions; Classified or vitrified waste materials; Aqueous scrub solution	Inorganics and some organics in liquids and contaminated soils	Long-term stability unknown; High energy requirements, especially with high soil water contents and low permeability; Electrical shorting caused by buried metal drums; Possible underground fires from combustible materials; Volatile metals near surface may volatilize; Site may require run-off controls
<b>Fixation/encapsulation</b> Lime solidification (Silicate)	In-tank; In situ	Storage; Immobilization	Leachates; Hazardous volatile emissions; solidified waste materials	Metals, waste oils, and solvents	Long-term stability unknown; Incompatible with borates, sulfates, carbohydrates; Requires complete and uniform mixing of soils and reagents; May reduce soil permeability and increase run-off
Thermoplastic Microencapsulation	In-tank; In situ	Volume Reduction; Storage; Immobilization	Leachates; Hazardous volatile emissions; Encapsulated waste materials	Complex, difficult to treat hazardous wastes	Wastes not treatable: Wastes with high water content, strongly oxidizing contaminants, anhydrous inorganic salts, tetraborates, iron and aluminum salts, and organics with low molecular weights and high vapor pressures; Long-term stability unknown; Requires complete and uniform mixing of soils and reagents; May reduce soil permeability and increase run-off



which may include equipment for surface applications, injection and recovery wells, and holding tanks for storing elutriate for reapplication.<sup>3,23</sup>

*System variables:* Variables affecting application of the technique include concentration and volume of contamination, distribution coefficients, interactions of flushing solution with soil, and suitability for installation of wells, drains, etc. for delivery and recovery.

*Design:* Design factors include sizing the delivery and recovery systems, and ensuring complete recovery of elutriate by use of drains, pumping wells, etc.

*Special application:* Use of soil flushing in a treatment train with bioremediation has been evaluated by Dworkin et al.<sup>134</sup> and by Kuhn and Piontek<sup>98</sup> for wood preserving contaminated sites. Flushing using surfactant/polymer combinations was used to remove high concentrations of PAH compounds; residual low concentrations were treated using biological processes.

## **Innovative Technologies**

### **Radio Frequency Heating**

*System description:* In situ radio frequency heating is performed by energizing the soil with electromagnetic energy in the radio frequency band.<sup>135</sup>

*System components and operation:* The energy is deposited by means of an electrode array placed in bore holes in the soil. The array is covered with a vapor barrier for the containment and collection of gases and volatilized contaminants. Equipment requirements include a transmitter, a power source, electrodes, ancillary equipment for gas extraction and containment, and soil boring devices.<sup>3</sup>

*System variables:* The frequency of the applied power is selected from the band reserved for the industrial, scientific and medical (ISM) communities by the Federal Communications Commission. The specific frequency is selected based on the dielectric properties of the soil, the depth of treatment required, and the size of the heated volume.<sup>135</sup>

*Design:* Design information includes type and homogeneity of soil, contaminants present, dielectric properties of soil, and frequency selection.<sup>135</sup>

*Special application:* The feasibility of the process for decontamination of soils contaminated with jet fuel and chlorinated solvents was recently demonstrated in bench- and pilot-scale experiments and at a U.S. Air Force field site.<sup>135</sup> In bench- and pilot-scale experiments, 90 percent to 99 percent removal of tetrachloroethylene and chlorobenzene from spiked sandy soils was seen, after the soils were heated to 88° to 160° C for periods of 14 to 40 hours. Chemical mass balance determinations were performed for the pilot-scale experiments (6-ft. columns of soil). Mass balance closure of 75 percent to 104 percent was demonstrated in most experiments. Uniform decontamination occurred along the length of the soil bed.

Jet fuel-contaminated soil was also heated in 6-ft tall columns. Ninety to 99 percent of total non-aromatics were removed from the soil by treatment at 150° C for a period of 14 to 40 hours.

Results from field testing the process at a U.S. Air Force site contaminated with jet fuel and solvents indicated 90 percent and 99 percent removal of total aliphatics and total aromatics, respectively.

PCB removal (72 percent to 99 percent) from spiked soils has also been demonstrated. However, mass balance calculations showed poor recoveries at higher (i.e., 300° C) temperatures than lower (i.e., 150° C) temperatures.

The RF in situ heating technique may also be used to enhance the performance of other remediation technologies, such as the K-PEG technique, which is a chemical dechlorination process.

### **Colloidal Gas Aphrons**

*System description:* Introduction of microscopic bubbles of gas (gas aphrons) into the soil adds oxygen to soil, delivering oxygen at concentrations greater than the water solubility, so that the liquid solution remains saturated with oxygen. The oxygen serves as the terminal electron acceptor for aerobic degradation of organic contaminants.<sup>3</sup>

*System components and operation:* An injection plow is used to inject colloidal gas aphrons (CGAs) in the soil. Exogenous reagents include the CGA microdispersion media and nutrients to sustain microbial activity.<sup>3</sup>

*System variables:* Soil texture and depth of contamination will affect distribution of CGAs through the contaminated matrix. Potential aerobic biodegradability of the contaminant is also important.

*Design:* Design aspects relate to components of the microdispersion generator, delivery system to the soil, volume of contamination, and distribution of the microdispersion through the contaminated volume.

*Special application:* Application has been limited to bench- and pilot-scale studies for phenol degradation.<sup>136</sup> No field-scale demonstration has been conducted.<sup>3</sup>

### **Electrokinetics**

*System description:* an electrokinetic phenomenon referred to as electroosmosis occurs when a liquid migrates through a charged porous medium under the influence of a charged electrical field.<sup>97</sup> The charged media are clays and sands that carry negative surface charges.

*Components and operation:* An electric field is created through the use of anodes and cathode. An extraction well (cathode) is used as the electric field that induces water to flow.

*System variables:* Important variables include soil type and texture, type of contaminants present, and hydraulic conductivity.

*Design:* Design requirements include knowledge of area and depth of contamination to determine placement of the electric field, water flow rates to determine rate of contaminant removal, and electrical power needs.

*Special application:* The technology has been evaluated for chrome removal by Horng and Banerjee.<sup>137</sup> Ionic metal species that are subject to ionic reactions and can migrate in the soil system appear to be types of contaminants that can be effectively treated with electrokinetics.<sup>3</sup>

### **Prepared Bed Reactors**

In a prepared bed system, the contaminated soil may be either: 1) physically moved from its original site to a newly prepared area, which has been designed to enhance remediation and/or to prevent transport of contaminants from the site; or 2) removed from the site to a storage area while the original location is prepared for use, then returned to the bed, where the treatment is accomplished. Preparation of the bed may consist of such activities as placement of a clay or plastic liner to retard transport of contaminants from the site, or addition of uncontaminated soil to provide additional treatment medium.

Possible prepared bed reactor technologies are identified in Table XIV and are evaluated with regard to function as

well as application and limitations. Treatment of contaminants with a prepared bed may be based on the techniques previously identified and described for in situ treatment.

An example of the use of a prepared bed reactor for soil remediation was described by Lynch and Genes.<sup>95</sup> Prepared bed treatment of creosote-contaminated soils from a shallow, unlined surface impoundment was demonstrated at a disposal facility for a wood-preserving operation in Minnesota. The contaminated soils contained creosote constituents consisting primarily of PAHs at concentrations ranging from 1,000 to 10,000 ppm. Prior to implementation of the full-scale treatment operation, bench-scale and pilot-scale studies simulating proposed full-scale conditions were conducted to define operation and design parameters. Over a four-month period, 62 percent to 80 percent removal of total PAHs were achieved in all test plots and laboratory reactors. Two-ring PAH compounds were reduced by 80–90 percent, 3-ring PAHs by 82–93 percent, and 4+-ring PAHs by 21–60 percent.

The full-scale system involved preparation of a treatment area within the confines of the existing impoundment. A lined waste pile for temporary storage of the sludge and contaminated soil from the impoundment was constructed. All standing water from the impoundment was removed, and the sludges were excavated and segregated for subsequent free oil recovery. Three to five feet of "visibly" contaminated soil was excavated and stored in the lined waste pile. The bottom of the impoundment was stabilized as a base for the treatment area. The treatment area was constructed by installation of a polyethylene liner, a leachate collection system, four feet of clean backfill, and addition of manure to achieve a carbon:nitrogen ratio of 50:1. A sump for collection of stormwater and leachate and a center pivot irrigation system were also installed. The lined treatment area was required because the natural soils at the site were highly permeable. A cap was also needed for residual contaminants left in place below the liner. Contaminated soil was periodically applied to the treatment facility and roto-tilled into the treatment soil. Soil moisture was maintained near field capacity with the irrigation system. During the first year of operation, greater than 95 percent reductions in concentration were obtained for 2- and 3-ring PAHs. Greater than 70 percent of 4- and 5-ring PAH compounds were degraded during the first year. Comparison of half-lives of PNAs in the full-scale facility were in the low end of the range of half-lives reported for the test plot units. Only two PNA compounds were detected in drain tile water samples, at concentrations near analytical detection limits.

Prepared bed treatment of a Texas oil field site with storage pit backfill soils contaminated with styrene, still bottom tars, and chlorinated hydrocarbon solvents was demonstrated on a pilot scale.<sup>94</sup> The remediation efforts included biological, chemical and physical treatment strategies. The pilot-scale, solid-phase biological treatment facility consisted of a plastic film greenhouse enclosure, a lined soil treatment bed with an underdrain, an overhead spray system for distributing water, nutrients, and inocula, an organic vapor control system consisting of activated carbon absorbers, and a fermentation vessel for preparing microbial inoculum or treating contaminated leachate from the backfill soils. Soils were excavated from the contaminated area and transferred to the treatment facility. Average concentrations of volatile organic compounds (VOCs) were reduced by more than 99 percent during the 94-day period of operation of the facility; most of the removal was attributed to air stripping. Biodegradation of semivolatile compounds reduced average concentrations by 89 percent during the treatment period.

#### In-tank Reactors

Specific in-tank reactor technologies are identified in Table XV and are evaluated with regard to functions, applica-

tion and limitations, and possible residuals and/or transformation products. Treatment of contaminants with in-tank reactors may be based on the techniques previously identified and described for in situ and prepared bed treatment. In addition to conventional reactors for treating contaminants removed from soils<sup>138</sup> and modified saturated/slurry systems,<sup>139</sup> unsaturated or solid-phase reactors are also applicable (e.g., composting reactors using white rot fungus to degrade organic contaminants<sup>140</sup>).

Additional information concerning in-tank treatment applications can be found in publications by Rich and Cherry<sup>25</sup> and by the U.S. EPA.<sup>28</sup>

#### Thermal Treatment

Thermal treatment is a in-tank process that utilizes high temperatures as the primary method for the destruction or detoxification of hazardous wastes. The destruction and removal efficiency (DRE) achieved for wastes incinerated in properly operated thermal processes often exceeds 99.99 percent. Available air pollution control technologies can effectively address the potential for particulate emissions. Thermal processing techniques that can potentially be used for the treatment of contaminated soils include: 1) fluidized bed incineration; 2) rotary kiln incineration; 3) pyrolytic incineration; and 4) vitrification. Short descriptions of each of the technologies are presented in Table XVI. Additional information concerning experience in incineration of solid materials at Superfund sites has been compiled by the U.S. EPA.<sup>141</sup> An authoritative and comprehensive review of incineration was presented by Oppelt<sup>142</sup> as part of the 1987 A&WMA Critical Reviews program.

#### Additional Issues and Research Needs

##### Degradation Under Anoxic Conditions in Soil

The author of this review is presently addressing research needs concerning bioremediation of contaminated soils, specifically degradation of organic chemicals under anoxic conditions in soils. In some contaminated soil environments, as a result of rapid consumption of oxygen by aerobic microorganisms and slow recharge rates of atmospheric oxygen into soil (i.e., in an anoxic environment), mineralization of organic chemicals will depend upon microbial utilization of electron acceptors other than molecular oxygen. In some cases where O<sub>2</sub> is not available, nitrate (NO<sub>3</sub><sup>-</sup>), iron (Fe<sup>3+</sup>), man-

**Table XV.** Critical environmental factors for microbial activity.<sup>24,54,59,122</sup>

Environmental factor	Optimum levels
Available soil water	25–85% of water holding capacity; –0.01 MPa
Oxygen	Aerobic metabolism: Greater than 0.2 mg/L dissolved oxygen, minimum air-filled pore space of 10% by volume; Anaerobic metabolism: O <sub>2</sub> concentrations less than 1% by volume
Redox potential	Aerobes and facultative anaerobes: greater than 50 millivolts; Anaerobes: less than 50 millivolts pH
ph	5.5–8.5
Nutrients	Sufficient nitrogen, phosphorus, and other nutrients so not limiting to microbial growth (Suggested C:N:P ratio of 120:10:1)
Temperature	15–45° C (Mesophiles)

ganese ( $Mn^{2+}$ ), and sulfate ( $SO_4^{2-}$ ) can act as electron acceptors if the organisms present have the appropriate enzyme systems.

Recent reports indicate that iron and manganese are not only important microbial electron acceptors in surface and subsurface environments, but may successfully compete with sulfate and carbon dioxide as electron acceptors.<sup>143-144</sup> Concentrations of iron and manganese in soils are significant, with levels from 20 to 3000 ppm for manganese and 3.8 to 5.2 percent for iron.<sup>145</sup> Demonstration of the presence of requisite microorganisms in the subsurface and the absence of microbial toxicity is necessary, but not sufficient, to evaluate whether biological activity is potentially important. Specific additional information that can be obtained as part of a site characterization for in situ treatment include identification of electron acceptor(s) present, amounts of electron acceptor(s) present, and redox and pH information to determine the chemical form of electron acceptors present. The information can be used in thermodynamic calculations to estimate the potential for biodegradation and the mechanism(s) influencing biodegradation.<sup>146</sup>

**Table XVI.** Thermal treatment techniques potentially applicable to the remediation of contaminated soils.<sup>29</sup>

Thermal treatment techniques	Description of process
Fluidized bed incineration	Utilization of a turbulent bed of inert granular materials (sand or contaminated soil) to improve transfer of heat; Air is blown through bed until materials are "suspended" and able to move and mix like a fluid, resulting in intimate contact of waste constituents with heated bed materials; Units operate at low combustion temperatures
Rotary kiln incineration	Utilization of a long inclined tube that is rotated slowly as contaminated soils and fuels are introduced to the high end of the kiln, resulting in improved combustion
Pyrolysis	Chemical decomposition of waste brought about by heating contaminants in the absence of oxygen; system involves use of two combustive chambers: in the first, wastes are heated to separate volatiles from nonvolatile char and ash, either by direct or indirect heating; in the second, volatile components are burned
Infrared incineration	Infrared radiators act as heat source to pyrolyze solids; Off-gases are burned by introduced air in secondary chamber

There is currently a lack of information concerning anoxic reactions in soil systems, even though the existence of anaerobic microsites under uncontaminated conditions are generally accepted by soil scientists. Mihelcic and Luthy<sup>147</sup> have evaluated the degradation of the hydrocarbons naphthalene and acenaphthalene under anoxic conditions, and Sullita and co-workers<sup>124-126</sup> have evaluated anaerobic degradation of chlorinated organic compounds.

Knowledge concerning potential anoxic reactions and rates of biodegradation in contaminated soil systems is needed to allow an evaluation of degradation, transformation, and detoxification systems that can be used for in situ treatment of chlorinated and non-chlorinated contaminants in contaminated soil systems. This type of information would be especially useful where large amounts of soil are contaminated at low levels and groundwater contamination is not likely. The reactions are also applicable to prepared bed and in-tank reactors where environmental conditions are controlled to facilitate treatment.

## Other Issues and Research Needs

Additional critical issues and research needs concerning soil remediation techniques at uncontrolled hazardous waste sites are related to levels of cleanup achievable and/or appropriate for a technique, i.e., the potential for specific remedial techniques to achieve specified regulatory clean-up requirements. Additional specific needs include, but are not limited to:

- effectiveness of microorganism seeding, as demonstrated by well-designed studies (including appropriate controls), to assess effectiveness
- evaluation of immobilization techniques for long-term stability and effectiveness
- development of cost information for comparison of remediation techniques
- development of treatment trains that are appropriate for different site scenarios
- identification of site characterization information that is critical for the selection of appropriate remedial actions.

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## References

1. R. M. Hall, Jr., N. S. Bryson, "Comprehensive environmental response, compensation, and liability act (Superfund)," in *Environmental Law Handbook*, 8th ed., G. J. Arbuckle, Ed., Government Institutes, Rockville, MD, 1985.
2. Public Law 99-499, "Superfund Amendments and Reauthorization Act of 1986," U.S. Government Printing Office, Washington, DC.
3. "Handbook on In Situ Treatment of Hazardous Waste-Contaminated Soils," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, EPA/540/2-90-002, January, 1990.
4. "National oil and hazardous substance pollution contingency plan; proposed rule," U.S. Environmental Protection Agency, 53 FR (Federal Register) 51394, December 21, 1988.
5. "Seminar on Site Characterization for Subsurface Remediations," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma and the Center for Environmental Research Information, Cincinnati, OH, CER-89-224, September, 1989.
6. "Site Characterization for Subsurface Remediations," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma and the Center for Environmental Research Information, Cincinnati, OH (in Press), 1990.
7. M. R. Scaff, D. C. Draper, "RSKERL-Ada Superfund Technology Support Center: The First Two Years," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, November, 1989.
8. "Superfund Innovative Technology Evaluation (SITE) Program," U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, EPA/540/8-89/010, November, 1989.
9. D. Scanning, "Assessment of international remedial technologies for application to Superfund sites," in *Proceedings of Second International IGT Symposium on Gas, Oil, Coal, and*

- Environmental Biotechnology*, New Orleans, LA, December 11-13, Institute of Gas Technology and Gas Research Institute, Chicago, IL, 1989, ch. 2.
10. "Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater," U.S. Environmental Protection Agency, *Proceedings and Appendices, Third Internatl. Conf., NATO Committee on Challenges of Modern Society (CCMS)*, Montreal, Canada, November 6-9, 1989.
  11. "Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International, Atlanta, Georgia, June 19-21: Technical Papers," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, EPA/540/2-89/056, 1989.
  12. "First International Conference on Contaminated Soil," TNO/BMFT, Kluwer Academic Publishers, Hingham, MA, 1985.
  13. "Second International Conference on Contaminated Soil," TNO/BMFT, Kluwer Academic Publishers, Hingham, MA, 1988.
  14. "Proceedings: International Conference on New Frontiers for Hazardous Waste Management, Pittsburgh, PA." U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, 1985.
  15. "Proceedings: Second International Conference on New Frontiers for Hazardous Waste Management," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, 1987.
  16. "Proceedings: Third International Conference on New Frontiers for Hazardous Waste Management," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, 1989.
  17. "Assessment of International Technologies for Superfund Applications: Technology Review and Trip Report Results," U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, EPA/540/2-88/003, 1988.
  18. "Assessment of International Technologies for Superfund Applications-Technology Identification and Selection," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, EPA/600/2-89/017, 1989.
  19. T. H. Pfeiffer, D. R. West, "Technology transfer in the U.S. Environmental Protection Agency's Hazardous Waste Office," *JAPCA* 40: 171 (1990).
  20. J. Lehr, "The misunderstood world of unsaturated flow," *Groundwater Monitoring Review*, Spring, 4, (1988).
  21. "Bioremediation of Hazardous Waste Sites Workshop," U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., and Center for Environmental Research Information, Cincinnati, OH, CERI-89-11, February, 1989.
  22. J. L. Sims, R. C. Sims, J. E. Matthews, "Bioremediation of Contaminated Soils," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/600/9-89/073, August, 1989.
  23. "Review of In-Place Treatment Techniques for Contaminated Surface Soils," U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Cincinnati, OH, EPA-540/2-84-0003a, September, 1984.
  24. R. C. Sims, D. L. Sorensen, J. L. Sims, J. E. McLean, R. Mahmood, R. R. Dupont, "Review of In-Place Treatment Technologies for Contaminated Surface Soils-Volume 2: Background Information for In-Situ Treatment," U.S. Environmental Protection Agency, Risk Reduction Research Laboratory, Cincinnati, OH, EPA-540/2-84-003b, 1984.
  25. G. Rich, K. Cherry, *Hazardous Waste Treatment Technologies*, Puvan Publishing Co., Northbrook, Illinois, 1987 ch. 7.
  26. "Technology Screening Guide for Treatment of CERCLA Soils and Sludges," U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C., EPA/540/2-88/004, September, 1988.
  27. R. C. Sims, J. L. Sims, "Cleanup of contaminated soil," in *Utilization, Treatment, and Disposal of Waste on Land*, K. W. Brown, B. L. Carlile, R. H. Miller, E. M. Turlledge, E. C. A. Runge, Eds., Soil Science Society of America, Wisconsin, 1986, p. 257.
  28. "Corrective Action: Technologies and Applications," U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, EPA/625/4-89/020, September, 1989.
  29. "A Compendium of Technologies Used in the Treatment of Hazardous Wastes," U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, EPA/625-8-87/014, 1987.
  30. "The Superfund Innovative Technology Evaluation Program: Technology Profiles," U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response and Office of Research and Development, Washington, DC, EPA/540/5-89/013, November, 1989.
  31. "Experience in Incineration Applicable to Superfund Site Remediation," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, and Center for Environmental Research Information, Cincinnati, OH, EPA/625/9-88/008, December, 1988.
  32. R. R. Dupont, R. C. Sims, J. L. Sims, D. L. Sorensen, "In Situ biological treatment of hazardous waste-contaminated soils," in *Bioremediation Systems*, D. L. Wise, Ed., CRC Press, Florida, 1988, ch. 2.
  33. "Hazardous Waste Land Treatment," U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C., SW-874, 1983.
  34. "Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations," U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C., EPA-530/SW-86-032, 1986.
  35. J. E. Bailey, D. F. Ollis, *Biochemical Engineering Fundamentals*, Second Edition, McGraw-Hill, New York, NY, 1986.
  36. *Wastewater Engineering: Treatment, Disposal, and Reuse*, Metcalf and Eddy, Inc., McGraw-Hill, New York, NY, 1979.
  37. R. A. Corbitt, *Standard Handbook of Environmental Engineering*, McGraw-Hill, New York, NY, 1989.
  38. L. D. Benefield, J. F. Judkins, D. L. Weand, *Process Chemistry for Water and Wastewater Treatment*, Prentice-Hall, Inc., Englewood Cliffs, NJ, 1982.
  39. R. Willis, W. W.-G. Yeh, *Groundwater Systems Planning and Management*, Prentice Hall, Inc., Englewood Cliffs, NJ, 1987.
  40. J. T. Wilson, L. E. Leach, J. Michalowski, S. Vendegrift, R. Callaway, "In Situ Bioremediation of Spills from Underground Storage Tanks: New Approaches for Site Characterization, Project Design, and Evaluation of Performance," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/600/2-89/042, September, 1989.
  41. R. C. Sims, W. J. Doucette, J. E. McLean, W. J. Grenney, R. R. Dupont, "Treatment Potential for 56 EPA Listed Hazardous Chemicals in Soil," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/600/6-88/001, April, 1988.
  42. R. Loehr, "Treatability Potential for EPA Listed Hazardous Chemicals in Soil," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/600/2-89/011, 1989.
  43. A. Sabljic, "Predictions of the nature and strength of soil sorption of organic pollutants by molecular topology," *J. Agric. Food Chem.* 32: 243 (1984).
  44. A. Sabljic, "On the prediction of soil sorption coefficients of organic pollutants from molecular structure: application of molecular topology model," *Environ. Sci. Technol.* 21: 358 (1987).
  45. A. Leo, C. Hansch, D. Elkins, "Partition coefficients and their uses," *Chem. Rev.* 71: 525 (1971).
  46. P. Nkedi-Kizza, P. S. C. Rao, J. W. Johnson, "Adsorption of Diuron and 2,4,5-T on soil particle separates," *J. Environ. Qual.* 12: 195 (1983).
  47. R. Mahmood, *Evaluation of Enhanced Mobility of PAHs in Soil Systems*, Ph.D. Dissertation, Department of Civil and Environmental Engineering, Utah State University, Logan, UT, 1989.
  48. R. J. Mahmood, R. C. Sims, "Mobility of organics in land treatment systems," *J. Environ. Eng.* 112: 236 (1986).
  49. P. S. C. Rao, A. G. Hornsby, D. P. Kilcrease, P. Nkedi-Kizza, "Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: model development and preliminary evaluation," *J. Environ. Qual.* 14: 376 (1985).
  50. R. C. Borden, P. B. Bedient, "In situ measurement of adsorption and biotransformation at a hazardous waste site," in *Subsurface Flow and Contamination Methods of Analysis and Parameter Uncertainty*, M. A. Marino, Ed., AWRA Monograph Series No. 8, Amer. Water Resources Assoc., Bethesda, MD, 1987, p. 629.
  51. C. D. Palmer, "Characterization of subsurface physicochemical processes," in "Seminar on Site Characterization for Subsurface Remediations," U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, CERI-89-224, 1989.
  52. A. L. Baehr, "Selective transport of hydrocarbons in the unsaturated zone due to aqueous and vapor phase partitioning," *Water Resour. Res.* 23: 1926 (1987).
  53. D. K. Kremer, E. P. Weeks, G. M. Thompson, "A field technique to measure the tortuosity and sorption-affected porosity for gaseous diffusion of materials in the unsaturated zone with experimental results from near Barnwell, South Carolina," *Water Resour. Res.* 24, 331 (1988).
  54. E. A. Paul, F. E. Clark, *Soil Microbiology and Biochemistry*, Academic Press, Inc., San Diego, California, 1989.
  55. B. E. Rittmann, P. L. McCarty, "Model of steady-state biofilm kinetics," *Biotechnol. Bioeng.* 22: 23 (1980).
  56. R. S. Horvath, "Microbial co-metabolism and the degradation of organic compounds in nature," *Biotechnol. Rev.* 36: 146 (1972).

57. J. J. Perry, "Microbial cooxidation involving hydrocarbons," *Microbiol. Rev.* 43: 59 (1979).
58. J. Keck, R. C. Sims, M. Coover, K. Park, B. Symons, "Evidence of cooxidation of polynuclear aromatic hydrocarbons in soil," *Water Res.* 23: 1467 (1989).
59. M. L. Rochkind, J. W. Blackburn, G. Saylor, "Microbial Decomposition of Chlorinated Aromatic Compounds," U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, EPA/600/2-86/090, 1986.
60. K. S. Park, R. C. Sims, W. J. Doucette, J. E. Matthews, "Biological transformation and detoxification of 7,12-dimethylbenz(a)anthracene in soil systems," *J. Water Pollut. Control Fed.* 60: 1822 (1988).
61. B. D. Symons and R. C. Sims, "Assessing detoxification of a complex hazardous waste using the Microtox™ bioassay," *Arch. Environ. Contam. Toxicol.* 17: 497 (1988).
62. R. C. Sims, J. L. Sims, R. R. Dupont, "Human health effects assays," *J. Water Pollut. Control Fed.* 60: 1093 (1988).
63. T. M. Vogel, C. S. Criddle, P. L. McCarty, "Transformations of halogenated aliphatic compounds," *Environ. Sci. Technol.* 21: 722 (1987).
64. M. M. Fogel, A. R. Taddeo, S. Fogel, "Biodegradation of chlorinated ethenes by a methane-utilizing mixed culture," *Appl. Environ. Microbiol.* 51: 720 (1986).
65. S. Hartsmans, J. A. M. deBont, J. Tramper, K. Ch. M. A. Luyben, "Bacterial degradation of vinyl chloride," *Biotechnol. Letters* 7: 383 (1985).
66. *Toxicity Testing Procedures Using Bacterial Systems*, D. Liu, B. J. Dutka, Eds., Marcel Dekker Inc., New York, NY, 1984.
67. B. J. Dutka, G. Bitton, *Toxicity Testing Using Microorganisms*, CRC Press, Inc., Boca Raton, FL, 1986.
68. B. N. Ames, J. McCann, E. Yamasaki, "Methods for detecting carcinogens and mutagens with the Salmonella/mammalian-microsome mutagenicity test," *Mutation Res.* 31: 347 (1975).
69. D. M. Maron, B. N. Ames, "Revised methods for the Salmonella mutagenicity test," *Mutation Res.* 113: 173 (1983).
70. R. C. Sims, J. L. Sims, R. R. Dupont, "Human health effects assays," *J. Water Pollut. Control Fed.* 56, 791, (1984).
71. R. C. Sims, J. L. Sims, R. R. Dupont, "Human health effects assays," *J. Water Pollut. Control Fed.* 57: 728 (1985).
72. R. C. Sims, J. L. Sims, R. R. Dupont, "Human health effects assays," *J. Water Pollut. Control Fed.* 58: 703 (1986).
73. R. C. Sims, J. L. Sims, R. R. Dupont, "Human health effects assays," *J. Water Pollut. Control Fed.* 59: 601 (1987).
74. J. R. McCann, J. R., R. Choi, E. Yamasaki, B. N. Ames, "Detection of carcinogens as mutagens in the Salmonella/microsome test: Assay of 300 chemicals," *Proc. Natl. Acad. Sci.* 72: 5135 (1975).
75. A. A. Bulich, "Use of luminescent bacteria for determining toxicity in aquatic environments," in *Aquatic Toxicology*, L. L. Markings, R. A. Kimerle, Eds., American Society for Testing and Materials, Philadelphia, PA, 1979, p. 98.
76. J. E. Matthews, A. A. Bulich, "A toxicity reduction test system to assist predicting land treatability of hazardous wastes," in *Hazardous and Industrial Solid Waste Testing: Fourth Symposium*, STP-886, J. K. Petros, Jr., W. J. Lacy, and R. A. Conway, Eds., American Society of Testing and Materials, Philadelphia, PA, 1984, p. 176.
77. J. E. Matthews, L. Hastings, "Evaluation of toxicity test procedure for screening treatability potential of waste in soil," *Toxicity Assessment: Internatl. Quarterly* 2: 265 (1987).
78. D. E. Armstrong, J. G. Konrad, "Nonbiological degradation of pesticides," in *Pesticides in Soil and Water*, W. D. Guenzi, Ed., Soil Science Society of America, Madison, Wisconsin, 1974, ch. 7.
79. C. Abbott, R. C. Sims, "Use of bioassays to monitor polycyclic aromatic hydrocarbon contamination in soil," in *Superfund '89, Proc. 10th National Conf.*, Hazardous Materials Control Research Institute, Silver Spring, Maryland, 1989, p. 23.
80. "Guide for Conducting Treatability Studies under CERCLA," U.S. Environmental Protection Agency, Office of Solid and Emergency Response and Office of Research and Development, Washington, DC, Contract No. 68-03-3413, November, 1989.
81. M. P. Coover, R. C. Sims, W. J. Doucette, "Extraction of polycyclic aromatic hydrocarbons from spiked soil," *J. Assoc. Offic. Anal. Chem.* 70: 1018 (1987).
82. K. S. Park, R. C. Sims, R. R. Dupont, W. J. Doucette, J. E. Matthews, "Fate of PAH compounds in two soil types: influence of volatilization, abiotic loss and biological activity," *Environ. Toxicol. Chem.* 9: 187 (1990).
83. A. S. Donagan Jr., P. S. C. Rao, "Overview of terrestrial processes and modeling," in *Guidelines for Field Testing Soil Fate and Transport Models*, S. C. Hern, S. M. Melancon, Eds., U.S. Environmental Protection Agency, Environmental Monitoring Systems, Las Vegas, NV, 1986, p. 1-1.
84. D. C. Digulio, I. H. Suffet, "Effects of physical, chemical, and biological variability in modeling organic contaminant migration through soil," in *Superfund '88, Proc. 9th National Conf.*, Hazardous Materials Control Research Institute, Silver Spring, MD, 1988, p. 132.
85. J. Weaver, C. G. Enfield, S. Yates, D. Kraemer, D. White, "Predicting Subsurface Contaminant Transport and Transformation: Considerations for Model Selection and Field Validation," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/600/2-89/045, August, 1989.
86. T. E. Short, "Modeling processes in the unsaturated zone," in *Land Treatment: A Hazardous Waste Management Alternative*, R. C. Loehr, J. F. Malina, Eds., The University of Texas at Austin, TX, 1986, p. 211.
87. "Interactive Simulation of the Fate of Hazardous Chemicals during Land Treatment of Oily Wastes: RITZ User's Guide," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/600/8-88-001, 1988.
88. W. A. Jury, W. F. Spencer, W. J. Farmer, "Behavior assessment model for trace organics in soil: model description," *J. Environ. Qual.* 12: 558 (1983).
89. J. E. McLean, R. C. Sims, W. J. Doucette, C. L. Caupp, W. J. Grenney, "Evaluation of mobility of pesticides in soil using U.S. EPA methodology," *J. Environ. Eng.* 114: 689 (1988).
90. D. K. Stevens, W. J. Grenney, Z. Yan, "User's Manual: Vadose Zone Interactive Processes Model," Utah State University, Logan, UT, 1988.
91. D. K. Stevens, W. J. Grenney, Z. Yan, R. C. Sims, "Sensitive Parameter Evaluation for a Vadose Zone Fate and Transport Model," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/600/2-89/039, 1989.
92. B. D. Symons, R. C. Sims, W. J. Grenney, "Fate and transport of organics in soil: model predictions and experimental results," *J. Water Pollut. Control Fed.* 60: 1684 (1988).
93. W. J. Grenney, C. L. Caupp, R. C. Sims, T. E. Short, "A mathematical model for the fate of hazardous substances in soil: model description and experimental results," *Hazard. Wastes & Hazard. Materials* 4: 223 (1987).
94. W. D. St. John, D. J. Sikes, "Complex industrial waste sites," in *Environmental Biotechnology—Reducing Risks from Environmental Chemicals through Biotechnology*, G. S. Omenn, Ed., Plenum Press, New York, NY, 1988, p. 163.
95. J. Lynch, B. R. Genes, "Land treatment of hydrocarbon contaminated soils," in *Petroleum Contaminated Soils, Vol. 1: Remediation Techniques, Environmental Fate, and Risk Assessment*, P. T. Kostecki, E. J. Calabrese, Eds., Lewis Publishers, Chelsea, MI, 1989, p. 163.
96. D. Ross, T. P. Marziarz, A. L. Bourquin, "Bioremediation of hazardous waste sites in the USA: case histories," in *Superfund '88, Proc. 9th National Conf.*, Hazardous Materials Control Research Institute, Silver Spring, Maryland, 1988, p. 395.
97. L. Murdoch, B. Patterson, G. Losonsky, W. Harrar, "Innovative Technologies of Delivery or Recovery: A Review of Current Research and a Strategy for Maximizing Future Investigations," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, Contract 68-03-3379, 1988.
98. R. C. Kuhn, K. R. Piontek, "A Site-Specific In Situ Treatment Process Development Program for Wood Preserving Site," *Proceedings of Oily Waste Fate, Transport, Site Characterization, and Remediation*, Technical Assistance Program of U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, May 17-18, 1989.
99. R. R. Dupont, J. A. Reineman, "Evaluation of Volatilization of Hazardous Constituents at Hazardous Waste Land Treatment Sites," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA 600/2-86/071, 1986.
100. R. Unterman, D. L. Bedard, M. J. Brennan, L. H. Bopp, F. J. Mondello, R. E. Brooks, D. P. Bobley, J. B. McDermott, C. C. Schwartz, and D. K. Dietrich, "Biological approaches for polychlorinated biphenyl degradation," in *Environmental Biotechnology—Reducing Risks from Environmental Chemicals through Biotechnology*, G. S. Omenn, Ed., Plenum Press, New York, NY, 1988, p. 253.
101. *Pesticides in Soil and Water*, W. D. Guenzi, Ed., Soil Sci. Soc. Am., Madison, WI, 1974.
102. C. A. I. Goring, D. A. Laskowski, J. W. Hamaker, R. W. Mickle, "Principles of pesticide degradation in soil," in *Environmental Dynamics of Pesticides*, R. Haque, W. H. Freek, Eds., Plenum Press, New York, NY, 1975.
103. N. J. Hutzler, B. E. Murphy, J. S. Gierke, "State of Technology Review: Soil Vapor Extraction Systems," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, EPA/600/2-89/024, January, 1990.
104. W. F. Spencer, M. M. Cliath, W. J. Farmer, "Vapor density of soil-applied dieldrin as related to soil-water content, temperature and dieldrin concentration," *Soil Sci. Soc. Amer. Proc.* 33:

- 509 (1969).
105. W. F. Spencer, W. J. Farmer, M. M. Cliath, "Pesticide volatilization," *Residue Rev.* 49: 1 (1973).
  106. J. J. Johnson, R. J. Sterrett, "Analysis of in situ air stripping data," *Proceedings of the 5th National Conference on Hazardous Waste and Hazardous Materials*, Hazardous Materials Control Research Institute, Las Vegas, NV, April, 1988, p. 451.
  107. R. L. Johnson, "Soil vacuum extraction: laboratory and physical model studies," *Proceedings of the Workshop on Soil Vacuum Extraction*, U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, April 27-28, 1989.
  108. D. C. Diguilio, J. S. Cho, R. R. Dupont, M. W. Kembrowski, "Conductance of Field Tests for Evaluation of Soil Vacuum Extraction Applicability and Design," U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, 1990.
  109. R. Miller, *Evaluation of Enhanced Biodegradation using Soil Venting as an Oxygen Source*, Ph.D. Dissertation, Department of Civil and Environmental Engineering, Utah State University, Logan, UT, 1990.
  110. R. Hinchee, "Enhanced biodegradation through soil venting," *Proceedings of the Workshop on Soil Vacuum Extraction*, U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, April 27-28, 1989.
  111. R. Hinchee, D. Downey, "In situ enhanced biodegradation of petroleum distillates in the vadose zone," *Proceedings of International Symposium on Hazardous Waste Treatment: Treatment of Contaminated Soils*, Air and Waste Management Association, U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, February 5-8, 1990.
  112. "Demonstration Bulletin: In Situ Vacuum Extraction, Terra Vac, Inc.," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, EPA/540/M5-89/003, 1989.
  113. "Cleanup of Releases from Petroleum USTs: Selected Technologies," U.S. Environmental Protection Agency, U.S. Environmental Protection Agency, Office of Underground Storage Tanks, Washington, DC, EPA/530/UST-88/001, 1988.
  114. L. G. Wilson, "Monitoring in the vadose zone: Part III," *Ground Water Monitoring Review*, Winter 155, (1983).
  115. L. G. Wilson, "Monitoring in the vadose zone: Part I, Storage changes," *Ground Water Monitoring Review*, (Fall), 32, (1981).
  116. L. G. Wilson, "Monitoring in the vadose zone: Part II," *Ground Water Monitoring Review*, (Spring), 31, (1982).
  117. *Proceedings of International Symposium on Hazardous Waste Treatment: Biosystems for Pollution Control*, Air & Waste Management Association and U.S. Environmental Protection Agency, Cincinnati, OH, February 20-23, 1989.
  118. *Proceedings of International Symposium on Hazardous Waste Treatment: Treatment of Contaminated Soils*, Air & Waste Management Association and U.S. Environmental Protection Agency, Cincinnati, OH, February 5-8, 1990.
  119. *Environmental Biotechnology—Reducing Risks from Environmental Chemicals through Biotechnology*, Omenn, G. S., Ed. Plenum Press, New York, NY, 505 pp.
  120. *Biotechnology Applications in Hazardous Waste Treatment*, G. Lewandowski, P. Armenante, B. Baltzis, Eds., Engineering Foundation, New York, NY, 1989.
  121. Hazardous Materials Control Research Institute, "Use of Genetically Altered or Adapted Organisms in the Treatment of Hazardous Wastes," Symposium, Hazardous Materials Control Research Institute, Silver Spring, Maryland, November 30-December 1, 1989.
  122. R. L. Huddleston, C. A. Bleckman, J. R. Wolfe, "Land treatment biological degradation processes," in *Land Treatment: A Hazardous Waste Management Alternative*, R. C. Loehr, J. F. Malina, Eds., University of Texas Press, Austin, TX, 1986, p. 41.
  123. M. R. Overcash, D. Pal, *Design of Land Treatment Systems for Industrial Wastes—Theory and Practice*, Ann Arbor Science, Ann Arbor, MI, 1979.
  124. J. M. Sufliata, J. M. Tiedje, "The anaerobic degradation of 2,4,5-trichlorophenoxyacetic acid by a dehalogenating bacterial consortium," Abstracts of the Annual Meeting, Amer. Soc. for Microbiol. Washington, DC, 1983, p. 266.
  125. J. M. Sufliata, A. Horowitz, D. R. Shelton, J. M. Tiedje, "Dehalogenation: a novel pathway for the anaerobic biodegradation of haloaromatic compounds," *Science* 218: 1115 (1982)
  126. J. M. Sufliata, J. A. Robinson, J. M. Tiedje, "Kinetics of microbial dehalogenation of haloaromatic substrates in methanogenic environments," *Appl. Environ. Microbiol.* 45: 1466 (1983)
  127. H. Kobayashi, B. E. Rittmann, "Microbial removal of hazardous organic compounds," *Environ. Sci. Technol.* 16: 170A (1982).
  128. B. Walton, T. A. Anderson, "Microbial degradation of trichloroethylene in the rhizosphere: Potential application to biological remediation of waste sites," *Appl. Environ. Microbiol.* 56: 1012 (1990).
  129. W. Aprill, R. C. Sims, "Evaluation of the use of prairie grasses for stimulating polycyclic aromatic hydrocarbon treatment in soil," *Chemosphere*, 20: 253 (1990).
  130. M. J. Cullinane, Jr., L. W. Jones, P. G. Malone, "Handbook for Stabilization/Solidification of Hazardous Wastes," U.S. Environmental Protection Agency, Hazardous Wastes Engineering Research Laboratory, Cincinnati, OH, EPA/540-2-86/001, 1986.
  131. J. B. Truett, R. L. Holberger, K. W. Barrett, "Feasibility of In Situ Solidification/Stabilization of Landfilled Hazardous Wastes," Contract No. 68-03-3665, U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Cincinnati, OH, 1983.
  132. "Technology Evaluation Report: SITE Program Demonstration Test, International Waste Technologies, In Situ Stabilization/Solidification, Hialeah, Florida, Volume 1," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, EPA/540/5-89/004a, 1989.
  133. R. Raghavan, E. Coles, D. Dietz, "Cleaning Excavated Soil Using Extraction Agents: A State-of-the-Art Review," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, EPA/600/2-89/034, 1990.
  134. D. Dworkin, D. J. Messinger, R. M. Shapot, "In Situ Flushing and Bioreclamation Technologies at a Creosote-based Wood Treatment Plant," *Proceedings of the 5th National Conference on Hazardous Wastes and Hazardous Materials*, Las Vegas, NV, Hazardous Materials Control Research Institute, Silver Spring, MD, April 19-21, 1988.
  135. H. Dev, J. Bridges, G. Sresty, J. Enk, N. Mshaiel, M. Love, "Radio Frequency Enhanced Decontamination of Soils Contaminated with Halogenated Hydrocarbons," U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH, EPA/600/2-89/008, 1989.
  136. D. L. Michaelsen, D. A. Wallis, F. Sebba, "In situ biological oxidation of hazardous organics," *Env. Prog.* 3: 103 (1984).
  137. J. Horng, S. Banerjee, "Evaluating Electro-Kinetics as a Remedial Action Technique," in *Proceedings, Second International Conference on New Frontiers for Hazardous Waste Management*, U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, EPA/600/9-87/018F, 1987, p. 65.
  138. E. K. Nyer, *Groundwater Treatment Technology*, Van Nostrand Reinhold Co., Inc., 1985.
  139. G. H. Brox, D. E. Hanify, "A new solid/liquid contact bioslurry reactor making bio-remediation more cost-effective," presented at the Colorado Hazardous Waste Conference, Denver, Colorado, November 6-7, 1989.
  140. M. J. McFarland, W. L. Aprill, X. J. Qiu, R. C. Sims, "Biological composting using the white rot fungus *Phanerochaete chrysosporium* for remediation of soil contaminated with wood preserving and petroleum waste organics," *Proceedings of the Institute of Gas Technology (IGT) Symposium on Gas, Oil, and Environmental Biotechnology*, New Orleans, LA, December 11-13, 1989.
  141. "Experience in Incineration Applicable to Superfund Site Remediation," U.S. Environmental Protection Agency, Risk Reduction Engineering Research Laboratory, EPA/625/9-88/008, 1988.
  142. T. Oppelt, "Incineration of hazardous wastes: A critical review," *JAPCA* 37: 585 (1987).
  143. D. R. Lovely, E. J. P. Phillips, "Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron and manganese," *Appl. Environ. Microbiol.* 54: 2415 (1988).
  144. D. R. Lovely, E. J. P. Phillips, D. J. Lonergran, "Hydrogen and formate oxidation coupled to dissimilatory reduction of iron or manganese by *Alternomonas putrefaciens*," *Appl. Environ. Microbiol.* 55: 700 (1989).
  145. W. L. Lindsay, *Chemical Equilibria in Soils*, John Wiley and Sons, Inc., New York, New York, 1979.
  146. M. J. McFarland, R. C. Sims, "A thermodynamic framework for evaluating PAH degradation in subsurface environments for use in site characterization," *Ground Water* (under review, 1990).
  147. J. R. Milhelcic, R. G. Luthy, "Microbial degradation of acenaphthene and naphthalene under denitrification conditions in soil-water systems," *Appl. Environ. Microbiol.* 54: 1188 (1988).

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