

**SITE REMEDIATION TECHNIQUES SUPPORTING ENVIRONMENTAL
RESTORATION ACTIVITIES: A REVIEW**

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ABSTRACT

A variety of techniques for environmental remediation have been compiled and summarized. The paper is intended to provide an overview of remediation methods currently utilized at various hazardous waste sites. Specific examples of method application are given when possible and references for each technique are provided should more detailed information be desired. Remediation methods, categorized as biological, chemical, or physical, are covered for contaminated soils and environmental waters.

INTRODUCTION

The literature contains a number of books, articles, and federal documents on various remediation techniques available for environmental restoration activities. However, a single document that is a compilation of the majority of methods utilized by United States federal agencies and the private sector for environmental remediation is not known to exist. The purpose of this paper, therefore, is to provide a comprehensive overview of the techniques and methods available for environmental remediation. It is not intended to provide in-depth detail for any one technique, but rather to serve as initial guidance for remedy selection alternatives and to act as a catalyst in option-specific literature searches. Because of their concise nature in the original form, some of the passages contained herein were taken from the primary works and have been appropriately referenced. While the author has attempted to construct a comprehensive manuscript, it is not intended to be viewed as all inclusive.

Treatment methods are divided into those for soil remediation and for surface and groundwater remediation. Further categorization results in the consideration of biological, chemical, and physical treatment techniques, with methods alphabetized within categories. Eighteen methods are reviewed that pertain to the remediation of soils (Table 1). Data on the treatment of ground and surface water is less voluminous; this paper reviews seven techniques for remediation of environmental waters (Table 2). The majority of techniques are categorized as physical treatments with only one process, biodegradation, falling under the biological treatment category. Chemical treatments involve the application of agents to promote extraction of the hazardous substance, and physical treatments involve removal of the hazard through physical means. The relative benefit of the various remediation methods has dependence in large-scale applicability as well as overall cost. Techniques such as in-situ vitrification can be applied only to finite areas in each application, however, because of the associated expense, multiple applications in different areas of the same waste site increase the method's cost-effectiveness. Figures 1 and 2 provide a summary of the degree of effectiveness, cost, technological development, and lasting effect for each soil and water remediation method, respectively.

Many of the remediation techniques summarized in this paper are still in the investigational stages and have been applied only in the laboratory or on a small scale. Techniques successful in the field are noted by inclusion of examples of large-scale application. The omission of such examples indicates the small- or bench-scale status of current work. Some techniques may be applicable only under certain environmental conditions; this relevance is explicitly stated for those methods. No information was found regarding post-treatment, site-specific ecological problems.

REMEDICATION OF SOILS

Biological Treatments

Biodegradation generally refers to the breakdown of organic compounds by living organisms eventually resulting in the formation of carbon dioxide and water or methane. Inorganic compounds are not biodegraded, but they can be biotransformed, that is, transformed into compounds having more or less mobility or toxicity than their original form. In many cases, the biodegradation processes involve a particular microorganism that attacks a specific molecular site. Complete and rapid biodegradation of many contaminants may require, not only specific environmental conditions, but also changing conditions to satisfy the needs of the microbe [1]. Tsang et al. [2] have investigated the mobility of several different metals in soil and the influence of the biodegradation process on that mobility. They have shown that active microorganisms influence the ability of soil to retain or release metals and that cysteine is an effective agent for the release of some metals from soil.

A Canadian commercial operation (Biogenie, Inc., Sainte-Foy, Quebec, Canada) utilizes an inexpensive, above-ground bioremediation technique. Hydrocarbon contaminants are removed from soils by bioremediation and volatilization. The potential of hydrocarbon biodegradation depends on the availability of desired microorganisms. Supplementing soils with prepared cultures is practiced when the indigenous content is low. Environmental conditions such as pH, temperature, oxygen, nutrients, and soil moisture also can influence biodegradation results. Air emissions from the "biopile" are treated by biofiltration where the pollutants are degraded and mineralized by heterotrophic aerobic microorganisms. A typical biopile system contains an asphalt or high-density membrane pad on which contaminated soils are stockpiled, an overhead spray irrigation system for optimizing soil moisture and adding nutrients to the soil, a drain system connected to a reservoir for leachate collection, a pump to force air through the pile for aeration, and an impermeable sheeting which covers the pile for air and moisture control [3].

Advantages of this technology include low land requirement, low capital and operating costs, and good process control. Cost of treatment depends on soil volume and treatment time, which typically ranges from \$50 to \$90/m³ of soil. This treatment method has removal efficiencies greater than 80% for mineral oil and grease products and greater than 95% for monocyclic aromatic hydrocarbons. Biodegradation rates for hydrocarbons under biopile treatment conditions have been reported as high as 44 kg/m³ per day. In addition, the process generates no liquid wastes and presents no risk of site contamination [3].

Chemical Treatments

Remediation Using Actinide Chelators. Gopalan et al. [4] are working to design and synthesize organic chelators for selective binding of actinide ions from soils and waste streams. Their studies show that multidentate oxoligands such as hydroxamate, iminodiacetate, and hydroxypyridinones are potential candidates for binding actinide ions present in acidic, aqueous solutions. They have also identified and synthesized chelating agents for plutonium. These chelators contain either a flexible acyclic structural backbone or a rigid benzene spacer to which the ligands are attached. Specific application under the complex conditions relevant to environmental remediation strategies for actinides is in an early stage of development. Potential solubility problems, stability, and pH requirements exist that could limit the use of chelators.

Chemical Immobilization. In-situ immobilization can be carried out by introducing treatment chemicals into the ground by various means. If soluble chemicals are used, they can be applied by saturating the soil with the chemical solution. This fluid application may be carried out at a high rate by surface flooding the site or more gradually by spraying and allowing the solution to drain freely into the soil. The variation in application rate will affect the period of soil exposure to the treatment material, the degree of void filling accomplished, and the amount of air present in the soil during the treatment period. A complementary confinement or pumping system may be appropriate if the soluble treatment chemical has undesirable environmental effects or is worth recycling due to high chemical costs [5].

Insoluble chemicals can be introduced into the ground by spreading, filling, forced injection, suspension transport, or by placing it in a low permeability encapsulation barrier. Spreading may suffice as a means of treating metals if the soil has a high moisture content and the metal contaminants lie close to the surface. This may be most applicable to soils with high organic content. Tilling is the most common method of introducing a soil chemical treatment into the ground. Routine tilling can mix dry chemical additives into the soil to a depth of one to two feet. Special deep tilling equipment is available which can reach as deep as five feet into the ground. Fine insoluble chemicals can be transported short distances through soil voids by placing them in suspension in water or in a weak solvent or acid. The suspension material is then injected in a fashion similar to chemical grouting or through nozzles in close spaced probes. Typically, fine material can be transported several feet from the nozzle in this fashion. The particle size can be correlated to soil grain size using traditional grouting guidelines. In formations with high permeability and low organic content where metals have migrated to depths greater than 10 feet or more, mixing insoluble treatment materials into the soil may be impractical. Under these

circumstances, the treatment chemical can be placed into a barrier material, such as bentonite soil or asphalt emulsions used for slurry wall construction, jet grouting, or block displacement [5].

Test results have demonstrated that with chemical treatment, heavy metal mobility is drastically reduced, and between 82 to 95 percent of the metals are confined to the part of the column containing chemical additives. The cost of in-situ immobilization typically range from \$13.9/ton to \$33.8/ton and include costs of chemical additives, soil preparation, and chemical additive application. This is a cost-effective alternative to alleviate metals, which will not present any adverse environmental or health hazards in their treated state. The cost of tilling in dry chemicals to soil has been estimated at \$0.42/ton [5]. Projects on a pilot field scale are needed to give a complete evaluation of the immobilization processes.

Critical Fluid Extraction. Organic compounds, primarily PCBs and PAHs, appear to be the most amenable to extraction from soils and sludges with a technique utilizing liquefied gas, typically carbon dioxide, propane, butane, and sometimes alcohol. High pressure and moderate temperatures are used to compress the gas to fluid state. At the critical temperature and pressure, where the fluid state occurs, the mass transfer capabilities of the "critical fluid" are at their best. The critical fluid extraction process begins with the addition of hazardous waste to a vessel containing a critical fluid. The organics move to the top of the vessel with the critical fluid and are pumped to a second vessel. There, the temperature and pressure are decreased causing the contaminants to volatilize from the critical fluid. The concentrated organics are then recovered and the critical fluid is recycled. Extraction efficiencies between 90 and 98 percent have been demonstrated using PCB-laden sediments. Volatile and semivolatile organics in liquid and semi-solid wastes have been removed with 99.9 percent efficiencies in the laboratory [6].

An estimate of performance and cost for the implementation of such a system can be developed with a bench- or pilot-scale test, and a full-scale design can be formulated from a successful pilot test. However, the cost of implementing this technology is generally high --\$100,000 to \$1,000,000 in 1990 dollars -- due to the complexity of the process and the need to maintain high pressures. This complexity also makes it difficult to predict the efficiency of the process. Finally, critical fluid extraction, together with treatment and disposal methods, can constitute a full and permanent solution to a contaminated site [6].

Oxidation. Oxidation, in waste remediation, refers to the movement of a contaminant to a more oxidized or more environmentally benign state. Oxidation technologies form part of the many treatment alternatives that have the capability to reduce or eliminate both the volume and toxicity of

contaminants. Three technologies are summarized that utilize oxidation as a treatment method: 1) chlorine dioxide and hydrogen peroxide additives, 2) photolysis, and 3) reductive dechlorination.

Chlorine dioxide and hydrogen peroxide are easy to incorporate into various environmental media under treatment, including water, waste water, leachate, air, and soil. Chlorine dioxide and hydrogen peroxide are frequently used as disinfectants, bleaching, and oxidizing agents. They can oxidize hazardous materials that are either organic or inorganic compounds. Sometimes when these oxidizing agents cannot completely degrade the contaminants, they can transform the contaminants into constituents that are amenable to other forms of degradation, such as biological processes.

Chlorine dioxide is usually best applied to an aqueous phase chemical for oxidation. Gas-gas and gas-solid reactions may be vigorous and even explosive if the concentrations are not uniformly distributed and if the temperature is not adequately controlled. The advantage of using chlorine dioxide over chlorine is that it does not readily add chlorine to organic compounds, it just oxidizes them. The cost to generate chlorine dioxide depends on the method used and the quantity required.

Hydrogen peroxide is utilized in environmental applications as a chemical oxidizing agent and as a source of oxygen. It effectively and easily oxidizes organic and ring compounds. It also is economical, easily available at low cost in a form ready for application. While it leaves no harmful by-products, slow and incomplete reactions with some species, such as saturated alkanes, have been documented. Because it is an oxygen source, hydrogen peroxide can be used in the subsurface for bioremediation applications.

Many organic compounds absorb light energy at visible or ultraviolet wavelengths. This energy promotes the decomposition of the chemical. Ultraviolet radiation is sufficient to cleave many types of covalent bonds. It has been shown to degrade PCBs, dioxins, PAHs, and several aromatic constituents of gasoline, including benzene, toluene, ethylbenzene, and xylene. This technique is advantageous in that organic waste is destroyed and the generated residuals are minimal. Although the application of photolytic treatments outside the lab has been limited, the results from the few pilot studies conducted are promising. Liquid, gaseous, and solid media are suitable to such treatment. For a technique to be effective, a high proportion of the surface area of the medium must be exposed to light. Ultraviolet light is sometimes used to intensify the oxidation process in the presence of the principal oxidizing chemicals, such as ozone or hydrogen peroxide.

Reductive dechlorination has been used on soil contaminated with PCBs and other organic chemicals. This process mixes contaminated liquids, soils, and sludges with an alkali-metal hydroxide reagent in a treatment reactor. Reductive dechlorination, like oxidation, modifies the

molecular structure of the contaminant such that the contaminant is transformed to a more benign substance. The treatment removes chlorine atoms from hydrogen-carbon molecules. These molecules are then amenable to destruction by means of biological treatment and other technologies. Before reductive dechlorination is implemented, bench- or pilot-scale testing should be conducted. Typical costs for this technique range between \$130 to \$390/m³ for soil. Since remediation of hazardous waste is a complex process, the oxidation technologies described above are often applied together [6].

In-Situ Catalyzed Peroxide Remediation. In-situ chemical oxidations have the potential for rapidly treating soils contaminated with toxic and persistent organic wastes. One mechanism for introducing strong oxidants into contaminated soils is the catalyzed decomposition of hydrogen peroxide to form the hydroxyl radical. Ho et al. [7] use an injector to introduce hydrogen peroxide below grade in an upward flow design for the remediation of soils. Their studies showed that a nitrobenzene contaminant was reduced in concentration by more than 50% over a 15-day period at depths below grade ranging from 15 to 66 centimeters. Injection pressure and injection depth influenced decontamination efficiency.

Based on results of laboratory studies, in-situ chemical oxidation appears to be a viable soil remediation technique that is dependent on the efficient delivery and distribution of hydrogen peroxide throughout the region to be treated. Initial results suggest that H₂O₂ injection into contaminated soil may also be successful in inaccessible contaminated sandy soil [7]. Gates et al. conducted bench-scale slurry studies using 0.3 L slurry reactors and trichloroethylene (TCE) concentrations in the 1.0 to 3.4 mg/kg range. TCE reductions as high as 98% of initial concentrations were achieved [8].

Photodegradation with Uranium Recovery. Dodge and Francis [9] have developed a process to recover toxic metals including uranium from soils using citric acid and visible light photodegradation. Early studies showed that the uranyl ion is photochemically active in the presence of organic acids, and on exposure to visible light, a uranyl citrate complex undergoes photochemical oxidation/reduction reactions. The studies of Dodge and Francis showed that, although the uranyl citrate complex is not biodegradable, the photochemical degradation results in the precipitation of uranium as an insoluble oxide. The citric acid and contaminated soil or sludge is first treated with bacteria which degrades, free of complexed citric acid, to carbon dioxide and water. The supernatant containing the uranium-citrate complex is then separated and subjected to photodegradation for uranium recovery.

The rate and extent of photochemical degradation of the uranyl citrate complex, as well as formation of intermediate and end products were influenced by the presence of oxygen and initial pH. The overall rate of photodegradation was faster at a pH of 3.5 than a pH of 6.0, and uranium precipitation was prevented by the absence of oxygen, excess citric acid, and intermediate degradation products.

Physical Treatments

Capping. Cover systems provide a stabilization mechanism by reducing the amount of water through-put in a burial trench or retention basin. The cover typically is composed of a surface layer that supports vegetation, a drainage layer, a low-permeability layer, and a gas-venting layer. The requirements of the site dictate which layers are necessary, and some sites will not need all layers. The surface layer is generally soil with adequate organic matter to sustain vegetation. This layer requires good drainage to support the vegetation's growth. The vegetation stabilizes the surface layer. To prevent harm to the lower layers of the cover, the vegetation must be of a type that has shallow roots and is adapted to the climate. The decomposition of organic matter results in the generation of methane gas. If uncontrolled, gas that migrates within the cover system can balloon and possibly combust. Therefore, the gas must be vented in a controlled manner [6].

Interim stabilization was successful at the Hanford site in an old PUREX chemical sewer liquid effluent ditch. Stabilization was carried out by a three phase process that included (1) scraping the surface soil from the sides of the ditch to its center, (2) backfilling the ditch with clean soil and regrading to a shallow slope, and (3) revegetating the entire area. The interim stabilization methods are expected to maintain the integrity of the ditch for at least a five-year period [10].

Cementitious Waste Forms. Sulfur polymer cement (SPC) has been used to stabilize high loadings of volatilized toxic metals. SPC is a sulfur composite material with a melting point of 110-120° C, that resists attack by most acids and salts. Studies show that the compound has a very long life and its strength greatly increases within the first few years after forming. Sulfur polymer cement concrete (SPCC) is also strong, with an average compressive strength of 4,000 psi, when the Nuclear Regulatory Commission (NRC) requires only 500 psi. The advantages of SPC are [11]: (1) it has a greater waste-to-agent ratio than concrete; (2) it has the ability to be remelted and reformed; (3) it is less permeable than concrete; (4) in its final waste form it is devoid of water; and (5) it can be processed at relatively low temperatures. In determining cost and environmental advantages, the volume-reduction factor offered by the sulfur polymer cement is its most redeeming aspect with the high cost of waste disposal. Additionally, the absence of water in the final waste

form offers less chemical breakdown, biodegradation, leaching, and gas generation after disposal. However, SPC is new and therefore, continued testing is essential.

Low-level radioactive wastes that have been separated from high-level wastes are being processed and stored in a waste form referred to as "saltstone". Saltstone is a mix of the low-level waste, cementitious blast furnace slag, and fly ash [12]. The saltstone is disposed of by emplacement or entombment in an engineered structure. The resulting structure is a large warehouse-size block of concrete that receives backfill on all four sides to bring its top level with the surface. A cap of gravel and clay is used to control runoff, and leachate monitors are put in place to monitor the structure's performance.

Electrokinetic Remediation. Investigators at Sandia National Laboratory [13] are researching an electrokinetic process for in-situ remediation of anionic contaminants. In electrokinetic remediation, electrodes are implanted in the soil and a direct current is imposed. Ionic species and charged particles in the soil water migrate toward one of the electrodes; the bulk water tends to migrate toward the cathode. Contaminants arriving at the electrodes then may be removed from soil by methods such as adsorption onto the electrode, precipitation at the electrode, pumping of water near the electrode, or complexing with ion-exchange resins.

Electrokinetics offers the possibility of inducing a greater flow through fine-grained soils, creating contamination movement that could not otherwise be achieved [14]. Results seem to indicate an optimum soil moisture content between 14 and 18 weight percentage exists for electromigration. The process also appears to be a low-cost alternative to other technologies (about \$1/ton of contaminated media), especially in clays where pump and treat methods are not effective [15]. Although the results of various studies suggest electrokinetics as a promising technology, further testing is needed at both laboratory and field levels to develop it fully for site remediation [14].

Incineration Technologies. Several types of incinerators are reviewed, including: the rotary kiln, infrared furnaces, liquid injection, plasma arc, fluidized bed, and the multiple hearth. Hazardous wastes can be volatilized and combusted in incinerators at temperatures that range from 870 to 1,200° C. Incineration at these temperatures can break the chemical bonds of organic compounds and other substances. Incineration reduces the risks posed by hazardous wastes because they efficiently destroy chemical contaminants, thereby reducing the toxicity and volume of substances at hazardous waste sites. The toxicity of radioactive contaminants, however, would not be eliminated by incineration, although bulk volumes may be reduced. In general, the waste's matrix influences the technical complications and the economics of incineration.

The rotary kiln is the most versatile of incinerators, capable of burning a broad range of hazardous and non-hazardous liquids, solids, and slurries. It burns liquid or solid wastes efficiently because, as the cylindrical combustion chamber rotates, wastes become well mixed with oxygen. However, gaseous wastes are not usually processed in kilns because they must be fed at a higher rate, and the residence time available is generally insufficient for complete oxidation. Liquid and solid wastes can be burned simultaneously. Typical feed rates for solid wastes are 160 to 175 grams per second. Liquid wastes are atomized with steam or air and burned in suspension in the main combustion chamber. The feed rate for the atomized waste stream typically ranges between 170 and 620 cm³/sec. Capital and costs for the rotary kiln are usually higher than for other types of incinerators [16].

In the infrared conveyor furnace (ICF), energy in the infrared region is used to heat waste to a specific temperature where desorption and/or incineration of the organic contaminants occurs. The gases that are exhausted from the furnace carry the desorbed contaminants and are combusted in a secondary combustion chamber [6]. When properly designed and operated, infrared conveyor furnaces have demonstrated their ability to exceed the following destruction and removal efficiencies (DRE): 1) Toxic Substances Control Act (TSCA) standard of 99.9999% DRE for PCBs; 2) Resource Conservation and Recovery Act (RCRA) performance standard of 99.99% DRE for organic compounds; and 3) RCRA performance standard of 99.9999% DRE for dioxins and furans [16]. These systems have been used in a number of operations, ranging from pilot-scale units used to obtain TSCA permits or evaluate the technology to commercial incineration of large quantities of contaminated soil. The SITE (Superfund Innovative Technology Evaluation) Program demonstrated that an infrared conveyor furnace unit with nominal capacity to process 91 Mg/day would operate for \$165 to \$555 Mg/d (in 1990 dollars) [6].

A liquid injection incinerator is the most common type used for the incineration of hazardous wastes in the liquid form. With this technology, liquid, gaseous, or slurry waste is injected into the combustion chamber through a nozzle or burner. The nozzle mixes the liquid with air, atomizing it into a suspension of droplets that is quickly vaporized. Before a waste is fed into a liquid injection incinerator, pretreatment in the form of filtration, degassing, neutralizing, or mixing may be required, especially to reduce particles or to modify the viscosity of the liquid. High-viscosity wastes are often pretreated with in-line heaters or tank coils, or they are blended with a miscible liquid of lower viscosity [16]. The rate of feed for land-based liquid injection incineration systems ranges between 0.05 and 1.05 L/s, 0.16 L/s being a typical rate. Ocean-based liquid injection incinerators are advantageous because a higher rate of waste combustion can be utilized in the absence of strict stack emission regulations [6].

The carbon arc used primarily to cut and weld was the origin of the plasma arc technology used in incinerators today to create very high temperatures. A plasma is considered to be a partially ionized gas with sufficient energetic ions and electrons to produce a highly reactive environment. A plasma is created when gases are ionized while passing through an electric field that is strong enough to strip electrons from the molecules of the gas. The gas itself remains electrically neutral if it is made up of equal numbers of positively and negatively charged particles. When the ionized species in the plasma recombine with the stripped electrons, significant amounts of energy are released. This energy takes the form of heat and can be used for decomposing chemicals. The arc exposes contaminants to a high temperature for a relatively long period of time. The plasma arc furnace effectively destroys organic compounds in solid, liquid, or gaseous phases. However, the plasma arc furnaces achieve efficiencies only at high capital and operating costs, and high operating temperatures can lower the life of the construction materials. In general, plasma arc technology is still in the experimental phase [6].

The fluidized bed technology promotes turbulence and facilitates superlative mixing of the waste with hot air and hot media. The sustained agitation of the media allows larger waste particles to remain suspended until the combustion is complete, thus enhancing combustion efficiency. A fluid bed incinerator has a vertical refractory-lined reactor vessel containing a shallow bed of an inert granular material. Forced draft air is introduced at the bottom of the combustion chamber. As the air rises through a distribution plate and upward through the bed, it promotes strong agitation and causes the bed to mimic the physical properties of a liquid. The waste is injected radially into the preheated media, and combustion takes place within the bed as heat is transferred from the media to the waste. The fluidized bed technology offers high combustion efficiency; low maintenance; a versatile process suitable for solids, liquids, and gases; operation in continuous feed or batch mode; and low air requirements resulting in reduced costs for air emission control. Energy costs to operate this incinerator are particularly high [16].

The multiple hearth incinerator has been utilized for more than 60 years to burn sewage sludge. Studies have been conducted to determine its applicability for hazardous waste incineration. This technology consists of horizontal refractory-lined hearths arranged in a vertical structure. Rabble arms and teeth rotate on a central shaft to agitate and convey the waste through the incinerator. The liquid and gaseous wastes are injected into the top of the main chamber. The waste material enters the top hearth, and it is heated to combustion temperature by means of several ignition burners. Feed rates for sewage sludge vary between 9 and 16 g/m²/sec. The retention time for low-volatility compounds is usually higher in the multiple hearth unit than for other incinerators. For the disposal of excessively wet sludges, the multiple hearth is one of the most efficient incineration

technologies available. It also has high operating costs because the moving parts in the combustion chamber are expensive to maintain [16].

In-Situ Grouting. Over the long term, voids are created in the backfill and waste matrices of landfills, creating surface depressions and areas prone to water infiltration. In-situ grouting of shallow landfills [17] has been used to effectively control the inflow of surface water, thus reducing leach rates, into hazardous waste sites. Grouting, or the injection of matter to fill the voids, can be done with chemical grouts, in solution form, or slurry grouts that are in particulate form. Chemical grouts, such as sodium silicate or polyacrylamide, are introduced as liquids and form stable gels after injection. The chemical grouts have high penetration potential and can fill a waste trench as easily as water. Slurry grouts, those that are cement based or lime fly ash, consist of a liquid suspension of particles that harden into a solid mass after injection. Particulate grouts are limited to large void areas and cannot penetrate small voids or passages as easily as solution grouts. Chemical grouts are generally much more expensive and, unlike cements, their long-term stability is unknown.

The strength of fully permeated grouted soil depends on the specific grout used but also, density, average grain size, and grain size distribution of the soil. In general, strength increases with increasing density and decreasing effective grain size. Field pumping tests to determine feasibility and effectiveness must be carried out within the limitations that will be imposed by the job itself, in terms of the grout to be used and the pumping equipment [18].

In-Situ Vitrification. In-situ vitrification is the process of melting contaminated soil, buried wastes, or sludges in place to render the material nonhazardous. The vitrification process is based on the concept of heating the soil electrically to temperatures as high as 1,600 to 2,000° C. The high temperature destroys organic pollutants by pyrolysis. Most in-situ vitrification applications involve the melting of soils, however, process sludge, mill tailings, sediments, process chemicals, and other inorganics may also be treated effectively. Volume reduction of the soil matrix is about 20 to 40% and the process has been demonstrated at several Superfund sites. In-situ vitrification exhibits the following capabilities [6]: (1) the treatment process provides containment of organic, heavy metal, and radioactive wastes simultaneously; (2) the process reduces the toxicity, mobility, and volume of the waste material; (3) the residual product is relatively innocuous; and (4) the technology can be applied to water, debris, and various soil types. While the vitrified product has superior long term characteristics and permanence [19], it is an expensive method to employ.

The process of in-situ vitrification (ISV) begins with four electrodes (in a square pattern) being inserted into the soil to the desired treatment depth. Since soil at ambient temperature does not have

sufficient conductivity, the process is initiated by placing a conductive mixture of flaked graphite and glass frit between the electrodes to act as the starting path for the electric circuit. A current passed between the electrodes through the graphite and frit path initiates the melting process. The graphite starter path is eventually consumed by oxidation and the current is transferred to the surrounding molten soil, which is then electrically conductive. As the melt grows downward and outward, the nonvolatile elements become part of the melt matrix and the organic compounds are destroyed by pyrolysis. Conductive currents within the melt uniformly mix materials that are present in the soil. When the desired melt depth and volume have been achieved, the electric current is discontinued and the molten volume is allowed to cool and solidify. A hood and exhaust system is placed over the treatment area during vitrification to collect combustion gases that escape to the atmosphere. Using this method, melt depths of up to 19 feet have been demonstrated [19].

Based on U.S. Environmental Protection Agency tests of the ISV product incorporating waste from a Superfund site, it has been shown to have excellent structural strength, averaging 10 times the strength of unreinforced concrete in tension and compression. Over 160 bench-, engineering-, pilot-, and large-scale ISV tests have been conducted and have demonstrated the general feasibility and widespread application of the process. When initially determining the feasibility of ISV for remediating a new waste/soil type, bench-scale tests are the smallest and most economical to perform [19].

At Oak Ridge National Laboratory, Tixier et al. [20] have investigated the use of in-situ vitrification for the remediation of pits and trenches used to dispose of radioactive liquid wastes. Luey et al. [21] have demonstrated a large-scale in-situ vitrification process on a site with heavy metal and radionuclide contamination that also contains combustible timbers. The presence of the timbers apparently caused no adverse condition during the 288 hour vitrification process which produced a soil block of about 11 meters in diameter and 4 meters in depth.

During vitrification studies by Spalding [22], it was noted that Cs-137 was volatilized to a greater degree than expected, particularly in the presence of chloride-containing species. Sodium chloride was found to be the most effective, resulting in volatilization of >99% of the Cs-137 by treatment at 1,000° C. In subsequent tests, the majority of the chloride-induced volatilization occurred between 800 and 1,000° C for samples of both soil and soil/limestone mixtures. Spalding [22] suggests similar methods may be used for the removal of Cs-137 from soils in light of cesium's strong and generally irreversible fixation to the clay mineral fraction of most soils.

Soil Washing. Soil washing as a volume reduction process is relatively new. Early efforts concentrated on extraction using aqueous solutions and ignored the physical separation/volume

reduction possibilities. Recognition of the practical value of separating contaminated soils grew during the mid-1980's, furthered by environmental restoration requirements in the United States. The soil washing process is by no means universal and varies in the selection of hardware, the sequence of the unit processes, and the chemical agents/additives used. However, most of the apparatus in common use has been borrowed from the minerals processing industry. In one application, the U.S. Environmental Protection Agency's mobile soil washing system [23], the first stage of the process removes coarse soil (known as physical washing) and then relies on a multiple-stage chemical extraction process for washing contaminants from the fine (< 2 mm) soil. A volume reduction washing unit [24] first heats the soil to 200° F and then washes it with water and a surfactant or other additive. Particle size separation then occurs where the large fraction (> 2 mm) is assumed to be clean. Several more steps are then followed in the process to remove the contaminated fines. Knowledge of the distribution of contaminants among the various particle-size fractions is key to predicting the effectiveness of the volume reduction process [25].

In 1988, the U.S. Environmental Protection Agency found that capital costs for a soil washing system with a typical rate of 18 Mg/hr ranged between \$3 and \$6 million. Operation fees charged for soil washing programs ranged from \$80 to \$170/Mg (1988 dollars), excluding costs for the disposal of sludge or wash water. The costs decreased as the volume of soil treated increased [6].

Physical soil washing, the separation of contaminant-laden fine particles, is generally cost effective only for soils that are less than about 20% fines. Soil washing techniques in some areas, particularly Europe, utilize particle separation with particles less than about 60-70 microns being disposed of as hazardous waste. Gombert [26] speaks of adapting the soil washing techniques to the removal of radioactive contamination at the Idaho National Engineering Laboratory, but also mentions the difficulties associated with such a task, including: (1) some soils and sludges containing radioactivity are as much as one-third fines (< 50 microns); (2) the contaminants may not exist as particulates, but rather are derived from aqueous solutions; and (3) many radionuclides contaminate soils at the atomic level by chemically binding to the soil. The potential for success of the technology is extremely site- and contaminant-specific.

A mobile washing system (Scientific Ecology Group, Oak Ridge, Tennessee) performs several stages of particle-size separation, surfactant washing, ion-exchange separation, and air drying. This system has a capacity of 2-4 tons per hour with a demonstrated reduction in lead concentrations of about a factor of 20 [27].

Soil surfactant washing refers to the treatment of excavated soil or other matrix with a surfactant solution. Soil surfactant flushing, on the other hand, refers to a similar process, but with soils

remaining in situ. The two technologies are not well developed but look promising for some applications [28]. Unlike solvents that dissolve a contaminant and put the contaminant into solution, surfactants are compounds that, in solution, reduce the surface tensions between liquids or between a liquid and a solid. Surfactants can effect this change because of their inherent molecular structure: one end of the surfactant's molecule is readily soluble in water and the other end is insoluble. Surfactants can thus release a contaminant from a particle in soil. Surfactants are added to water which is used to flush the soil. The water with the surfactant should improve both the detergency of the aqueous solutions and the efficiency with which organic compounds are transported in aqueous solutions. The treatment is more effective when a greater surface area of the soil particle is exposed. The process works best in sandy soils; its effectiveness decreases with soil particle size [6].

Surfactant washing can be done in a variety of ex-situ configurations that involve the physical washing or mixing of the soil with a surfactant solution that is later recovered. In-situ surfactant flushing involves the delivery of surfactant to the contaminated medium in place by irrigation or injection wells; recovery wells are used to extract the surfactant down-gradient from the injection wells. If the nature of the site permits, in-situ soil surfactant flushing can be utilized at significant cost reduction. If the domain of the contamination is well below the water table, in-situ flushing may be the only technology available since excavation may be impossible [28].

The range of applicability of surfactant flushing/washing is not universal; the contaminants must be hydrophobic. Suitable compounds include chlorinated pesticides, PCBs, semivolatiles, petroleum products, plasticizers, chlorinated solvents, and aromatic solvents. These methods are not suitable for removing inorganics and much of the equipment used for surfactant flushing/washing can be used for metals removal simply by using other reagents, such as chelating agents or acids. One very important factor in using the in-situ flushing technology is that all of the contaminant-laden surfactant must be recoverable [28]. A major concern with this technology is the possibility of pollutant-laden surfactant solution escaping capture by the recovery well(s) and moving off the site. This could result from either improper design or failure of the pump on the recovery well [16].

The use of additives in the washing process is generally undesirable. If the technique is efficient with the use of only water, additives should be avoided entirely. When additives are applied, they are typically contaminant-specific and are usually acids, bases/caustics, surfactants, or chelating agents. Acids and chelating agents are specific to metals, but the particular reagent necessary is dependent not only on the metal, but its chemical form or species. Caustics can improve the extraction of organic acids. Many organics, especially those of low solubility or high viscosity,

may require surfactants. Several examples of recent experiences with soil washing techniques are given in Griffiths [25].

Sorting Methods. On the Johnston Atoll, Bramlitt [29] reports of radiologically contaminated soils being sorted into clean or contaminated constituents, depending on predetermined radiation concentration levels. The sorting takes place on a conveyor belt that travels beneath radiation detectors; the contaminated soil is diverted into a packaging unit and clean soil is reused on the Atoll without restriction. Potentially contaminated soil is processed at a rate of 750 m³/week with a volume reduction between 95 and 99 percent.

Stabilization/Solidification. In terms of hazardous waste treatment, stabilization generally refers to those techniques that reduce a chemical or radiological hazard by converting the waste into its least soluble, mobile, or toxic form. The physical nature of the waste is not necessarily changed in the stabilization process. Solidification, however, refers to a binding or encapsulation of the waste into a high-integrity structure. Migration is restricted primarily by isolating the waste within an impervious capsule. In general, in-situ stabilization/ solidification (S/S) systems are less costly than removing waste for treatment. Though the field of S/S has lately begun to mature into an accepted remediation technology, no long-term data are available, as it has only been in practice for about 20 years [30].

Surface encapsulation is utilized to stabilize hazardous waste in high-performance containers designed to withstand the stresses of transportation, handling, and disposal. In one instance, the surface encapsulation process [31] entails fabricating high-performance modules that have a composite structure of selected organic resins. Wastes are processed in two-steps by agglomeration with polybutadiene and encapsulation within a polyethylene jacket. The polybutadiene resin is employed because of its durability, its resistance to corrosion, and its impermeability to leachates. Because of its core/jacket design, the encapsulated package is very strong, providing much greater load capacity than traditional containers.

Thermal Desorption. Thermal desorption is a process that uses high temperatures (usually below 400° C, however) to drive organics out of soil by volatilization. The method is done in the absence of oxygen and uses temperatures much less than that required for combustion. The organics, in a separate phase of the remediation, are then either destroyed or condensed. Thermal desorption is unlike the incineration process which heats the soil to higher temperatures in an oxygenated atmosphere which both volatilizes and combusts the organics simultaneously. Thermal desorption offers several advantages over incineration including a reduced amount of gases produced, thereby

reducing the size of the off-gas handling system. Additionally, the public is more accepting of the desorption approach over incineration [6, 32].

Studies indicate that minimum conditions for desorption are a temperature of 300° C and a residence time of 30 minutes. These conditions will result in the removal of 99% or more of contained polynuclear aromatic hydrocarbons (PAHs) and volatile compounds [32]. Properly designed systems can offer an effective and economical remedial alternative for the treatment of large volumes of contaminated materials. Additionally, both the contaminated site and the contaminated medium can be recycled or reclaimed for beneficial reuse. For most applications, the majority of the cost of implementation is attributable to air pollution controls [6]. The process of implementing thermal desorption technologies usually begins with bench-scale tests. These can be performed with a pilot furnace to determine the feasibility of the treatment [32]. Thermal desorption is currently being used at more than 40 sites [33].

Vapor Stripping. Soil vapor stripping or extraction is applicable to the removal of volatile and semivolatile organic compounds from the vadose zone. The technology involves the positioning of a well through the contaminated region and the use of a vacuum to draw air down through the soil and up the well. Vapor stripping is essentially the reverse technology of air sparging. The air extracted from the well is routed through a demister to remove excess water and then a bank of filters to remove the volatile organics, after which it is vented to the atmosphere. The environmental impacts of this technique are low and the costs are typically much lower than other technologies [33]. Soil vapor extraction techniques can be used with other soil remediation technologies including biodegradation, soil washing, air sparging, and groundwater pump and treat [6].

Large volumes of soils can be treated readily with soil vapor extraction (SVE) systems. They are also relatively easy to install and they utilize off-the-shelf equipment. Cleanup times are fairly short, and the hazardous material is removed from the soil and destroyed. However, a complex site may require that several sequential and/or simultaneous technologies be implemented for optimally effective cleanup. Mathematical modeling is used to determine feasibility, estimate costs and cleanup times, and plays a major role in the design of the pilot study and the full-scale remediation facility. The most cost-effective SVE system employing regenerative oxidation would cost approximately \$200,000 [34]. Soil vapor extraction is currently being used at more than 150 sites [33].

The range of applicability of soil vapor stripping is bounded by the following constraints [33]: (1) the chemicals to be removed must be volatile or at least semivolatile (a vapor pressure of 0.5 torr or greater); (2) the chemicals to be removed must have relatively low water solubility or the soil

moisture content must be quite low; (3) the contaminants to be removed must be above the water table or floating on it (in the case of light nonaqueous-phase liquids); and (4) the soil must be sufficiently permeable to permit the vapor extraction wells to draw air through all of the contaminated domain at a reasonable rate.

REMEDICATION OF SURFACE AND GROUNDWATER

Biological Treatments

Wilson and Clarke [33] define biodegradation as the breakdown of organic compounds by living organisms resulting in the formation of carbon dioxide and water or methane. Another way of defining biodegradation is the disappearance of environmentally undesirable properties of a substance. Biodegradation is different from biotransformation, the conversion of an organic compound into a large molecular structure or loss of a characteristic property with no decrease in molecular complexity. In biotransformation the toxicity, form, and mobility of the original compound is altered. This is true of biodegradation, too. Biodegradation is caused by microorganisms. These are bacteria, fungi, and microfauna (e.g. protozoans, some worms, and some insects). Microorganisms degrade substances using specific and non-specific processes. Specific processes refers to a microbe targeting a single site of a molecule as the pivotal action in biodegradation. Non-specific processes are those with a chain of microbial events in the biodegradation of waste. Degradation pathways are determined quite often by environmental conditions such as pH, molecular oxygen and nutrient conditions. For example, petroleum products are best degraded in the presence of oxygen, aerobic conditions. Highly halogenated compounds require anaerobic conditions to remove the halogens. The biodegradation of a particular waste may require a series of different environmental conditions for a variety of microorganisms to cause a cascade of reactions. The chlorinated compounds, for example, first require reductive dechlorination in anaerobic conditions followed by breakdown of organics in aerobic conditions.

The primary microorganisms for biodegradation are the bacteria. Bacteria are prokaryotes; they are unicellular organisms containing circular genetic material not enclosed by a nuclear membrane. They are often distinguished by their sources of energy and their electron acceptors for respiration. Bacteria that use light as a source of energy are called phototrophs. Some bacteria oxidize organic matter and are called heterotrophs. Others oxidize inorganic compounds; these are the lithotrophs or chemoautotrophic bacteria. Bacteria that use oxygen to accept the electrons generated in respiration are aerobic. Inorganic acceptors are used by anaerobic bacteria. There are others too:

iron reducers, sulfate reducers, and carbon dioxide reducers. Bacteria are able to biodegrade a broad range of wastes.

Fungi, a group of eukaryotic, heterotrophic organisms, are able to excrete enzymes that breakdown some exotic compounds, recalcitrant compounds, and large organic molecules not readily degraded by most bacteria. However, little is known about fungal adaptations and processes in degrading anthropogenic substances [16]. Microfauna can change the soil environment (bioturbation), aerate surface soils, dilute contaminant concentrations through mixing, modify other variables, and control other microorganisms through predation [33].

A particular example of customized bioremediation comes from Jarvinen et al. [35]. They note that chlorophenols, and particularly pentachlorophenol, have been used as wood preservatives. These preservatives have since found their way into surface and groundwater systems. In the environment, chlorophenols are recalcitrated due to the inadequate conditions for biodegradation or the absence of chlorophenol-degrading organisms. In treatment systems, chlorophenols can be degraded at ambient temperatures under aerobic or anaerobic conditions. Jarvinen et al. [35] demonstrated that aerobic fluidized-bed biodegradation using flavobacterium and rhodococcus bacteria produces an effluent with chlorophenol concentrations close to drinking-water quality.

Bioremediation of surface and groundwater will remain expensive for some time [16]. The heating of water prior to biological treatment has been a prerequisite and dramatically increases the treatment expenses [35]. Recent studies indicate that considerable potential exists for biological systems, but the many factors that influence degradation and the rate at which it occurs are largely unknown [36]. There has been little experience with in-situ biological treatment of contaminated groundwater, and there have been virtually no field applications [16]. Ex-situ treatment is typically more controllable and predictable and technically less complex than in-situ treatment [6].

Chemical Treatments

Electron-Beam Irradiation. When irradiated with electron beams, water produces free electrons and the free radicals $H\bullet$ and $OH\bullet$. These free radicals react with trichloroethylene and carbon tetrachloride and other organic contaminants rendering them harmless. The resultant products are CO_2 , H_2O , salts, and other compounds. High dose rates of electrons are less efficient than low dose rates due to radical recombination. Recent developments have led to the creation of pulsed linear induction accelerators which can deliver a lower dose rate than conventional electrostatic electron accelerators and single-pulse accelerators. These accelerators are also physically smaller,

modular, and more reliable than conventional electron accelerators. It is speculated that they will destroy chemicals more effectively, although this remains to be proven [37].

Electron beam technology has shown removal efficiencies up to 99.99% in full-scale operation and it has been accepted into the SITE (Superfund Innovative Technology Evaluation) Program [38]. Lab and pilot-plant studies have shown high energy electron-beam irradiation to be effective and economical for the removal of hazardous organic contaminants in water [37].

Mercury Extraction. There are many methods of extracting mercury from surface water. All are chemical except one physical extraction method, electroplating. The chemical methods include (1) precipitation of mercury from a caustic solution of mercuric sulfide in the presence of aluminum, (2) precipitation of mercuric oxide from caustic solutions, (3) solvent extraction of mercury ions using ion exchangers, and (4) the use of emulsion liquid membranes. In each of these four methods of mercury extraction, the remediation of one contaminated stream results in the formation of another, requiring either landfilling or additional aqueous stream treatment [39].

A microemulsion is an optically transparent, thermodynamically stabilized dispersion of two immiscible phases. It is a combination of an aqueous phase, organic phase, surfactants, and other additives. Emulsions have internal droplets which can interact with mercury and other metals such as gold and silver. Coarse emulsions have internal droplets of 1 mm, whereas microemulsions have internal droplets of 50 to 1,000 angstroms. The smaller internal droplet size and lower interfacial tensions of the microemulsions allows for faster metal extraction because of the greater surface area for mass transfer and reaction. Larson and Wiencek [39] used oleic acid in a microemulsion liquid membrane to extract mercury from water. The mercury is stripped from the microemulsion (once extracted) with a strong mineral acid such as nitric, hydrochloric, or sulfuric acid. They found extraction and stripping of mercury to be a function of pH and mercury, oleic acid, and modifier (surfactants and other additives) concentration. A microemulsion containing a cation exchanger reduces the mercury content of an aqueous phase from 500 ppm to 0.3 ppm, which is a 40-fold improvement over equilibrium extraction. Emulsion liquid membranes minimize equilibrium limitations inherent with conventional solvent extraction by combining extraction and stripping into one step [40].

Radiocolloid Treatment. A radiocolloid is a suspension of tiny radioactive particles in a medium such as water. Inorganic colloids are characterized by concentration, mineralogy, and radioactivity levels. Los Alamos National Laboratory's Mortandad Canyon in northern New Mexico has an aquifer containing these radiocolloids. Radiation levels have reached several hundred times background due to colloids of plutonium and americium. Nuttall and Kale [41] have developed a

process for in-situ colloid remediation using the phenomenon of polyelectrolyte capture. A polyelectrolytic solution is added to the medium containing the radiocolloid. Polyelectrolytes are positively charged polymers which attach to the negatively charged radiocolloids. The polymer agglomerations (polymer + radiocolloid) cluster together and fall out of the medium where they can be physically removed. Nuttall et al [42] have shown polyelectrolyte polymer treatment of colloids to be successful in laboratory column tests. Further field work is necessary to demonstrate this technology at an actual site. Currently, colloid migration in groundwater is an active area of research and the role and existence of radiocolloids is under further study.

Removal by Sorption to Organo-Oxides. Organo-oxide synthetic sorbents provide an organic phase able to bind nonionic organic substances. An organo-oxide synthetic sorbent forms when anionic surfactants adsorb onto oxides in an acidic environment. For this to happen the oxide must have a net positive charge. A pH less than the zero point of charge (the pH at which solid surface charges from all sources are zero) causes the oxide to take on positive charges. Park and Jaffe [43] found that sorption of anionic surfactants onto oxides is pH dependent and decreases as the pH increases. Additionally, partitioning of nonionic organic pollutants onto synthetic sorbents is linearly dependent on concentration of the pollutant and proportional to the adsorbed mass of the surfactant. The sensitivity of the organo-oxide synthetic sorbent to pH allows for a continuous flow water treatment plant. A low pH allows for formation of the organo-oxide and subsequent extraction of nonionic organics. A raised pH removes the surfactants with the nonionic organic from the oxide.

Even though organo-oxide sorbents may not be as efficient as other technologies in terms of the amount of water treated, they do have several advantages. They can be generated in-situ, selective removal of a specific contaminant may be accomplished if a specific surfactant that sorbs the contaminant is selectively used, and the solute that is removed from the water can be recovered if so desired [43].

Physical Treatments

Air Sparging/Air Stripping. Contaminated water can be remediated in the ground or above the ground. The technique of remediating the water in the ground is called air sparging. Air sparging actually refers to two different techniques, in-well aeration and air injection. The technique of remediating the groundwater above the ground is called pump and treat [44]. Water is pumped out of the ground and treated by air stripping or granular activated carbon absorption or both [33]. In-well aeration involves the placement of a well, a vertical narrow chamber, in the ground extending to a depth below the water table. There are screens at the top and bottom of the well which allow water

to enter. A compressor pumps air to the bottom of the well. The air rises and creates a circulation cell of water flowing into the well at the bottom and leaving at the top. Along the way up, the water absorbs oxygen causing volatilization of the contaminants. Additionally, oxygen promotes aerobic bacteria growth, thus enhancing biodegradation of contaminants [45]. Air injection is the direct injection of air into the aquifer. The air rises up through the vadose zone and eventually into an extraction well where volatilized contaminants can be removed. Isherwood et al. [46] have written about Lawrence Livermore National Laboratory's (LLNL) four-part strategy to clean-up contaminated groundwater. LLNL has devised a plan to study and characterize the hydrogeology of a site and conduct simulation extractions of groundwater. Johnson [47] explains that the effectiveness of remediation can vary tremendously depending on the portion of the hazardous waste path targeted.

Air sparging is a remediation technique whereby a gas, usually air, is injected through a well to an area beneath the water table. The pumped-in air then creates an airlift pump which forces deep groundwater to circulate, in effect, within the upper portions of the aquifer. The process aerates the water and removes volatiles. As mentioned above, the air sparging process can also be used in conjunction with biodegradation to provide increased oxygen for groundwater remediation [45, 47]. In addition to other widespread uses in the United States, Looney et al. have successfully utilized air sparging with horizontal wells for large-area remediation of volatile organics [48].

While in-well aeration avoids lifting water above ground for treatment and has the potential to be more cost-effective and efficient than conventional pump and treat methods, it shares some of the same limitations. In-situ air sparging also presents several risks of enhanced contamination. Due to the potential for loss of control of its processes, an air sparge system should never be installed without a pilot test. Contamination spreading as a result of the water table rising has been reported, and there is an apparent risk of off-site vapor migration. However, these problems can be mitigated at many sites [45]. There is a lack of knowledge regarding the efficiency with which oxygen is transferred to groundwater. This must be addressed if in-situ air sparging is to be proven effective [46]. Much remains to be learned about specific applications of in-well aeration.

Air stripping relies on the sorption processes to transfer contaminants from the liquid to the gas phase. With this technology, the contaminated liquid is brought in contact with ambient air and the organic contaminants are transferred to the air. The first air stripping operations were in lagoons where the stripping was effected with a simple source of aeration. Air was bubbled in from the bottom and the contaminants were transferred to the air bubbles and released to the atmosphere [6].

Air and steam stripping technologies are most effective with VOCs and ammonia. To achieve greater than a 90% percent removal efficiency, towers packed with a transfer medium are used [6]. Air stripping has been shown to be enhanced by the injection of hot air or by heating interstitial air in the soil prior to the extraction process. In addition to the processes involved in the basic air stripping method described above, additional processing is necessary for the steam produced by thermal heating. In one demonstration, radio-frequency heating of the soil resulted in VOCs being reduced by 98.1 to 99.9% over the course of 12.5 days [49].

Incineration Techniques. There are incinerators for liquids, solids, and sludge. The feasibility of incineration depends on both the chemistry and the matrix of the waste. Organic constituency determines the combustibility of the waste while ash and chloride content influence the volume and character of solid residuals and air emissions. Waste treatment requires individualistic attention; certain intermediates and products of combustion will damage some incinerators. Wastes not completely incinerated generate products of incomplete combustion (PICs) which are organics with different chemical structures and properties, often more toxic, like dioxins and furans. Emissions are a concern with wastes containing chlorinated hydrocarbons, heavy metals, and large quantities of sulfur. The generation of unwanted products of incineration can be minimized by adjusting temperature, residence time of the waste in the incinerator, turbulence, and oxygen injection in the incineration process. There are a variety of incinerator types available depending on the waste form. Wastes are evaluated in terms of their combustibility, water content, and viscosity. Soil and groundwater wastes require a greater heat input than petroleum wastes. All of the four basic types of incinerators --- the rotary kiln, liquid injection, fluidized bed, and multiple hearth --- accept liquid wastes. They all, however, operate at different temperatures. The rotary kiln has a rotating cylindrical chamber that mixes the waste causing liquids and solids to burn efficiently. It is the most versatile of incinerators, burning a spectrum of waste types. The liquid injection incinerator mixes liquid with air; the waste is injected through a nozzle where it is then atomized into a suspension of droplets. In the fluidized bed incinerator, forced air through a shallow bed of inert granular materials (silica or aluminum) creates sustained agitations of the media promoting turbulence and facilitating mixing. The multiple hearth incinerator is a series of hearths with devices to mix the waste. The waste is heated and burned with ignition burners [16].

SUMMARY

We have presented a compilation of hazardous waste remediation methods for contaminated soil and water. It is the result of a rather thorough literature review, but the author does not claim to have included all methods in use for soil and water remediation. Some methods are chemical specific, while others apply to a broad range of pollutants. Techniques covered for soil remediation included the general categories of biological, chemical, and physical treatments as well as the more specific extraction, immobilization, and thermal methods. Groundwater treatments are limited to air stripping, bioremediation, free-radical reactions, incineration, and specific contaminant removal methods for mercury, radiocolloids, and nonionic organic substances.

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CAPTIONS

Figure 1. Summary of soil remediation method characteristics.

(Note to the Editor: Figure 1 consists of 3 pages).

Figure 2. Summary of surface and groundwater remediation method characteristics.

Table 1. Soil remediation techniques reviewed.

Technique	References
• Biological Treatments	1, 2, 3
• Chemical Treatments	
- actinide chelators	4
- chemical immobilization	5
- fluid extraction	6
- oxidation	6
- peroxide remediation	7, 8
- photodegradation	9
• Physical Treatments	
- capping	6, 10
- cementitious waste forms	11, 12
- electrokinetics	13, 14, 15
- incineration	6, 16
- in-situ grouting	17, 18
- in-situ vitrification	6, 19 - 22
- soil washing	6, 16, 23 - 28
- sorting	29
- stabilization/solidification	30, 31
- thermal desorption	6, 32, 33
- vapor stripping	6, 33, 34

Table 2. Surface and groundwater remediation techniques reviewed.

Technique	References
• Biological Treatments	6, 16, 33, 35, 36
• Chemical Treatments	
- electron-beam irradiation	37, 38
- mercury extraction	39, 40
- radiocolloid treatment	41, 42
- sorption to organo-oxides	43
• Physical Treatments	
- air sparging/air stripping	6, 33, 44 - 49
- incineration	16

SOIL Remediation Techniques	Degree of Effectiveness	Cost	Technological Development/ Research Needs	Lasting Effect of Method
Biological Treatments	<ul style="list-style-type: none"> •Canadian operation removal efficiencies >80% for mineral oil & >95% for mono-cyclic aromatic hydrocarbons (HC) •HC biodegradation rates under biopile-- 44,000 g/m³/day 	<ul style="list-style-type: none"> •Canadian operation--inexpensive; cost of treatment depends on soil volume and treatment time; \$50-90/m³ of soil •Low land requirement, low capital & operating costs 		<ul style="list-style-type: none"> •Canadian operation generates no liquid wastes and presents no risk of site contamination
Chemical Treatments				
Remediation using Actinide Chelators	Potential solubility problems, stability, and pH requirements that could limit the use of chelators exist		Currently being studied; early stage of development	
Chemical Immobilization	Tests results demonstrated that with chemical treatment, heavy metals mobility was drastically reduced; 82-95% metals confined	<ul style="list-style-type: none"> •In-situ treatment--cost effective alternative to alleviate metals •Costs of in-situ immobilization range from \$13.9-\$33.8/ton •Costs of tilling dry chemicals to soil estimated at \$0.42/ton 	Projects on a pilot field scale, reproducing actual and environmental conditions, are needed to give a complete evaluation of immobilization/ stabilization processes	Immobilized metals will present no adverse environmental hazards in their treated state
Critical Fluid Extraction	<ul style="list-style-type: none"> •Extraction efficiencies between 90-98% demonstrated using PCB-laden sediments •Process is complex; predicting the efficiency of such extraction is difficult 	<ul style="list-style-type: none"> •Cost of implementation high (due to process complexity & maintenance of high pressures) •Cost to mobilize extraction system--\$100,000-1,000,000 (1990 dollars) or more 	<ul style="list-style-type: none"> •Estimate of performance and cost can be developed with a bench- or pilot- scale test •A full-scale design can be formulated from a successful pilot test 	The extraction process, together with treatment and disposal technologies, can constitute a full and permanent solution to the site's contamination
Oxidation <ul style="list-style-type: none"> •Chlorine Dioxide CD •Hydrogen Peroxide HP •Photolysis P •Reductive Dechlorination RD 	<ul style="list-style-type: none"> •Oxidation can reduce or eliminate volume & toxicity •CD best applied to aqueous phase chemicals •HP easily oxidizes organic and compound rings •UV shown to degrade PCB, dioxins, PAHs 	<ul style="list-style-type: none"> •Cost to generate CD depends on method used and quantity required •HP is economical •RD treatment costs range from \$130-\$390/m³; actual costs depend on characteristics of site and specific contaminants 	<ul style="list-style-type: none"> •Application of photolytic treatments outside the lab has been limited, but results from few pilot studies are promising •Before RD is implemented, bench- or pilot-scale testing should be conducted 	

In-Situ Catalyzed Peroxide Remediation	<ul style="list-style-type: none"> •Injection pressure and injection depth influenced decontamination efficiency •Nitrobenzene was reduced in concentration by >50% over 15 days 		<ul style="list-style-type: none"> •Initial results suggest H₂O₂ injection may be successful in inaccessible contaminated sandy soil •Lab study results-- technique appears to be viable dependent on efficient delivery & distribution of H₂O₂ throughout region 	
Photodegradation with Uranium Recovery	<ul style="list-style-type: none"> •Overall rate of photodegradation faster at pH 3.5 than 6.0 •Absence of O₂, excess citric acid, and intermediate degradation products prevented uranium precipitation 			
Physical Treatments				
Capping	<ul style="list-style-type: none"> •Interim stabilization successful at Hanford •If uncontrolled, methane gas that migrates within cover system can balloon and possibly combust 			Interim stabilization methods at Hanford site expected to maintain integrity of ditch for at least 5-year period
Cementitious Waste Forms Sulfur polymer cement concrete (SPCC) Sulfur polymer cement (SPC)	<ul style="list-style-type: none"> •NRC requires only 500 psi compressive strength and SPCC avg. is 4,000 psi •SPC resists attack by most acids and salts, less permeable than concrete 	SPC can be processed at relative low temperatures and reduces volume which saves money due to high cost of disposal	SCP is new and therefore continued testing is essential	SPC has very long life and strength greatly increases within the first few years after forming
Electrokinetic Remediation	<ul style="list-style-type: none"> •Results indicate optimum moisture content for soil between 14-18 weight % exists •Possibility of inducing greater flow thru fine-grained soils 	Process appears to be a low-cost alternative to other technologies (\$1/ton), especially in clays where pump and treat methods are not effective	Although results suggest electrokinetics is promising, further testing is needed at both lab and field levels to fully develop for site remediation	
Incineration Technologies <ul style="list-style-type: none"> •Rotary Kiln RK •Infrared Conveyor Furnaces ICF •Liquid Injection LI •Plasma Arc PA •Fluidized Bed FB •Multiple Hearth MH Feed Rates (FR) Destruction and Removal Efficiency (DRE)	<ul style="list-style-type: none"> •Incineration reduces volume & toxicity •RK solid waste feed rate 160-170 g/s •ICF DRE 99.9999% for PCBs •PA efficiency at high temperatures is exceedingly high •FB enhances efficiency (larger particles remain suspended until combustion) •MH FR 9-16g/m²/s 	<ul style="list-style-type: none"> •Waste's matrix influences technical complications and economics of incineration •Capital and costs for RK are usually higher •ICF with capacity to process 100 ton/day-- \$150/ton (1990 dollars) •PA achieve efficiencies only at high capital and operating \$ •FB high energy \$ •MH high operation \$ 	<ul style="list-style-type: none"> •ICF systems have been used in a number of operations, ranging from pilot-scale units used to obtain TSCA permits or evaluate technology to commercial incineration of large quantities of contaminated soil •Plasma arc technology is still experimental; most units are prototypes 	

In-Situ Grouting ISG	<ul style="list-style-type: none"> •ISG of shallow landfills has been used to effectively control inflow of surface water into hazardous and radioactive waste sites •Chemical grouts--high penetration potential 	Chemical grouts generally much more expensive than slurry grouts		Chemical grouts long-term stability is unknown, unlike cements
In-Situ Vitrification ISV	<ul style="list-style-type: none"> •Reduces toxicity, mobility, and volume of waste, and residual product rendered relatively innocuous •Volume reduction of soil matrix ~ 20-40% 	Expensive	Over 160 bench-, engineering, pilot-, and large-scale tests conducted and have demonstrated general feasibility and widespread application of ISV	Vitrified product has superior long-term characteristics and permanence compared to other technologies
Soil Washing	<ul style="list-style-type: none"> •Knowing distribution of contaminants among various particle-size fractions is key to predicting effectiveness •Mobile washing system capacity of 2-4 tons/hr demonstrated reduction in lead concentrations by factor of ~20 •Contaminants must be hydrophobic 	<ul style="list-style-type: none"> •Soil washing generally cost effective only for soils that are <~20% fines •USEPA found that capital costs for a 18 Mg/hr ranged between \$3-6 mill. and \$80-170/Mg for operating fees •Need more data to develop credible preliminary cost figures on surfactant washing and flushing operations under field conditions 	Soil surfactant washing and flushing technologies are not well developed; very little pilot-scale work has been done to date, but look promising for some applications	A major concern with in-situ surfactant flushing is the possibility of pollutant-laden surfactant solution escaping capture by the recovery well(s) and moving off the site. This could result from either improper design or failure of pump on the recovery well
Sorting Methods	Potentially contaminated soil is processed at a rate of 750m ³ /week with a volume reduction between 95 and 99%			
Stabilization/Solidification S/S	Polybutadiene resin used in S/S is durable, resists corrosion, and is impermeable to leachates	In situ S/S systems generally less costly than removal for treatment and replacement	The field of S/S has lately begun to mature into an accepted environmental technology	No long-term data available because technology practiced for only 20 years
Thermal Desorption	Advantage over incineration--reduced amount of gases produced, thereby reducing the size of the off-gas handling system	<ul style="list-style-type: none"> •Can be economically applied to contaminated soil in moderate to large volumes •Temperatures < than required for combustion 	<ul style="list-style-type: none"> •Full-scale constructions and full-scale designs supported by pilot or prototype test data have been developed •Being used at more than 40 sites 	
Vapor Stripping	<ul style="list-style-type: none"> •Large volumes can be readily treated, cleanup times short, toxic material removed and destroyed •Environmental impacts are low 	<ul style="list-style-type: none"> •Costs typically much lower than other technologies •Cost-effective system employing regenerative oxidation would cost ~\$200,000 	<ul style="list-style-type: none"> •Mathematical modeling plays major role in design of pilot study and design of full-scale remediation facility •Soil vapor extraction used at >150 sites 	

WATER Remediation Techniques	Degree of Effectiveness	Cost	Technological Development/ Research Needs	Lasting Effect of Method
Biological Treatments	<ul style="list-style-type: none"> •Specific environment governs success of process •Aerobic fluidized-bed had higher chloro-phenol loading rates and better quality effluent than those reported 	<ul style="list-style-type: none"> •Technique will remain expensive for some time •Heating of water has been prerequisite which radically increases costs 	<ul style="list-style-type: none"> •Little experience with in-situ bioremediation of groundwater, and virtually no field applications •Little is known about fungal adaptation and processes in degradation of anthropogenic substances 	
Chemical Treatments				
Electron-Beam Irradiation	<ul style="list-style-type: none"> •Low dose rates of electrons more efficient •E-beam technology has shown removal efficiencies up to 99.99% in full-scale operation 	(See Technological Development/Research Needs category)	<ul style="list-style-type: none"> •Promising technology •Shown to be effective and economical for removal of hazardous organic compounds through lab and pilot-plant studies 	
Mercury Extraction	Microemulsion containing a cation exchanger reduces mercury content of aqueous phase from 500 ppm to 0.3 ppm, a 40-fold improvement over equilibrium extraction	With each of the four methods mercury extraction, the remediation of one contaminated stream results in the formation of another, requiring landfilling or additional aqueous stream treatment		
Radiocolloid Treatment	In-situ colloid remediation process using polyelectrolyte capture successful in laboratory column tests		<ul style="list-style-type: none"> •Further work necessary to demonstrate at actual site •Because field experiments uncertain, colloid migration in groundwater is area of active research 	
Removal by Sorption to Organo-Oxides	Advantages: can be regenerated in-situ; selective removal achieved if specific surfactant that sorbs contaminant selectively is used; solute removed can be recovered		Batch and column experiments done to demonstrate use of organo-oxide for treatment of nonionic organic pollutants	
Physical Treatments				
Air Sparging/ Air Stripping In-Situ Air Sparging IAS Pump & Treat P&T	<ul style="list-style-type: none"> •Efficiency with which O₂ is transferred to groundwater must be addressed if IAS to be proven effective •Air and steam stripping technologies most effective with VOCs and ammonia 	In-well aeration (IAS) has potential to be more cost-effective and efficient than conventional P&T, however subject to similar limitations	<ul style="list-style-type: none"> •Much to be learned about in-well aeration •Because of potential for loss of control, air sparging systems should never be installed without a pilot test 	Some practitioners report contamination spreading due to a rise in the water table, and there is an apparent risk of off-site vapor migration. However, at many sites these risks can be mitigated

