# BIOREMEDIATION

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FIGURE 1. Laboratory studies in bioreactors usually precede actual soil treatment

Once considered unproven technology, bioremediation has now been accepted for many types of contaminated soil and water

azardous waste cleanup via bioremediation is gaining popularity. One reason is the high degree of public acceptance, relative to alternatives such as incineration. Another is the clearer picture of the costs and benefits of microbial degradation. In many cases, bioremediation offers the most cost-effective means of decontaminating a site.

Success in applying bioremediation requires the understanding and proper application of three separate areas of expertise: microbiology; legal and regulatory rules and guidelines, and engineering principles, including the combination of biotreatment and conventional processes.

Engineers involved in waste management and disposal should have a basic understanding of each of these areas. Case studies in the following pages will enhance this understanding.

## Microbiology

Biological studies can identify naturally occurring microorganisms or consortia of microorganisms that degrade specific pollutants and, more importantly, classes of pollutants. These studies also reveal degradation pathways, essential to assure detoxification and mineralization. These studies can also demonstrate how to enhance microbial activity, such as by the addition of supplementary oxygen and nutrients, and by the adjustment of pH, temperature, and moisture.

#### •Regulatory rules

Regulations impact bioremediation in four ways. First, regulation of naturally occurring or modified microorganisms by authorities such as the U.S. Environmental Protection Agency (EPA) remains uncertain, and could deter a technically promising bioremediation choice. Second, consent agreements may require specific time deadlines that may not be achievable by bioremediation. Third, the demonstration of the proposed system may depend, in the U.S., on the issuance of an RD&D (research, development and demonstration) permit.

Finally, regulations may require cleanup parameters achievable by competing technology - incineration, for example — yet these parameters may be too low to achieve cost-effectively by bioremediation. On the other hand, there are means to obtain certain variances that allow bioremediation to be used on certain types of wastes.

## Engineering

Finally, remediation of sites involves many choices and the evaluation of a diverse set of technologies. There are a variety of biological degradation methods that can be considered: in situ treatment; bioslurrying; bioventing

COMPARISON OF BIOLOGICAL TREATMENT TECHNOLOGIES		
TYPE/COST (\$/yd³)	ADVANTAGES	DISADVANTAGES
Land Treatment \$30 - \$90	<ul> <li>Can be used for in situ or ex situ treatment depending upon contaminant and soil type</li> <li>Little or no residual waste streams generated</li> <li>Long history of effective treatment for many petroleum compounds (gasoline, diesel)</li> <li>Can be used as polishing treatment following soil washing or bioslurry treatment</li> </ul>	<ul> <li>Moderate destruction efficiency depending upon contaminants</li> <li>Long treatment time relative to other methods</li> <li>In situ treatment only practical when contamination is within two feet of the surface</li> <li>Requires relatively large, dedicated area for treatment cell</li> </ul>
Bioventing \$50 - \$120	Excellent removal of volatile compounds from soil matrix      Depending upon vapor treatment method, little or no residual waste streams to dispose      Moderate treatment time      Can be used for in situ or ex situ treatment depending upon contaminant and soil type	Treatment of vapor using activated carbon can be expensive at high concentrations of contaminants  System typically requires an air permit for operation
Bioreactor \$150 - \$250	<ul> <li>Enhanced separation of many contaminants from soil</li> <li>Excellent destruction efficiency of contaminants</li> <li>Fast treatment time</li> </ul>	High mobilization and demobilization costs for small projects      Materials handling requirements increase costs      Treated solids must be dewatered

and others. Bioremediation can be effective as a pre- or post-treatment step for other cleanup techniques. The need for diverse technologies is illustrated below by examples of field projects from sites containing pentachlorophenol, creosote, polychlorinated biphenyls and petroleum hydrocarbons.

## The biological perspective

Degradation of pollutants by microorganisms requires a carbon source, electron acceptor, nutrients, and appropriate pH, moisture and temperature. The waste can be the carbon source or primary substrate for the organisms. Certain waste streams may also require the use of a cosubstrate to trigger the production of enzymes necessary to degrade the primary substrate; some wastes can be cometabolized directly along with the primary substrate.

Different types of microorganisms require different electron acceptors. The most common aerobic bacteria use oxygen as the acceptor. Anaerobic bacteria can use a variety of nitrates, sulfates or carbon dioxide. Phosphorus and nitrogen are also required nutrients for healthy microbial growth.

Most biological reactions take place within a narrow band of temperature and pH. A neutral pH (6.5–7.5) is typically required for optimal growth. Temperature affects both the kinetics of the biochemical reactions that destroy the waste and the growth of the organisms that perform the degradation. The aerobic processes used to degrade most organic wastes occur around 15–40°C.

#### Negotiating the legal hurdles

Regulatory constraints are perhaps the most important factor regarding the selection of bioremediation as a treatment process. Regulations that define specific cleanup criteria, such as land disposal restrictions under the U.S. Resource Conservation and Recovery Act (RCRA), also restrict the types of treatment technologies to be used. Other technologies, such as incineration, have been used to define the "best demonstrated available technology" (BDAT) for hazardous waste treatment of listed wastes.

The schedule for a site cleanup can also be driven by regulatory issues. A consent decree may fix the timetable for a site remediation, which may elimi-

Fullscale application

common in recent years

has only become

nate the use of bioremediation, or limit the application to a specific biological treatment technology.

A waste that is not hazardous in EPA's system may be considered as hazardous by local regulations. Many states now have *de minimus* cleanup standards for petroleum constituents commonly found at underground storage-tank sites, or for polynuclear aromatic hydrocarbons (PAHs) that are found in coal tar, creosote, and some petroleum compounds.

Voluntary remediation can trigger the need for storage and treatment permits under RCRA. In particular, an attempt to clean up a highly contaminated area at a plant site may trigger a RCRA permit and cleanup of the whole facility, which the responsible party may be unwilling to do. If treatment of a contaminated area is proposed, a permit must be obtained when RCRA wastes are present, unless the work is done in situ or under certain limited RCRA permit exemptions.

Thus, if soil contaminated with RCRA wastes, for example, is picked up and treated, a permit is necessary. Further, the material cannot be returned to the place from which it was excavated, and before disposal in a fully permitted site, the treatment must meet the stringent land-disposal criteria developed for process wastes using BDAT treatment. This interpretation of the hazard-ous-waste disposal rules has raised interest in treating wastes in place.

The microbes that are being considered for use in bioremediation may themselves require some sort of regulatory review. The Toxic Substances Control Act (TSCA) authorizes EPA to regulate a wide variety of chemical substances. In this context, "chemical substance" has been defined in a broad enough manner to include microorganisms for some situations. At this time, it appears that only genetically engineered organisms will be regulated.

#### The chemical engineering view

Engineering a bioremediation system involves a combination of theory, practice, and common sense. Traditional chemical engineering concepts can be used to describe the transport of contaminants in soil and groundwater, and the kinetics of biological reactions. The

absence of precise values for many of these design factors makes estimation and experimentation necessary.

Two factors typically limit the effectiveness of biological treatment processes: the rate of desorption from the contaminated media, and the kinetics of reaction of the contaminant with the microorganism. Understanding the rate-controlling step offers insight into the use of a particular bioremediation technology.

For example, many organic compounds are difficult to remove from soils that contain high clay fractions. The biological treatment of this material is limited by the rate of desorption of the contaminant from the soil particle. Soils of this type may require surfactants, and the use of a slurry reactor, to accelerate the desorption of the organic material; the alternative is a very long, expensive reaction time.

## A consent decree may fix the timetable for a site remediation

An initial site characterization provides baseline data for determining the effectiveness of the treatment methods and forms the basis for negotiating closure of the site with regulators. The information developed in this step should answer a number of questions that will assist in the selection of the most effective method of treatment.

Many consultants and engineers consider bioremediation when evaluating remedial alternatives. But they often neglect to collect the basic data required to determine its cost and effectiveness. A typical site investigation consists of tens or even hundreds of soil borings and groundwater samples that may be analyzed for pollutant types. However, the soil chemistry, soil properties, or indigenous bacterial population may not be determined. The following additional analyses should be performed if biological treatment is being considered as a remedial alternative:

- Soil pH
- Soil nutrients (N as NH<sub>3</sub>, P as PO<sub>4</sub>)

- Physical properties of soil (grain size distribution)
- Heterotrophic (i.e., nonphotosynthetic) bacterial plate count

These additional analyses are available from most laboratories at a nominal cost, typically on the order of \$200/sample for all four analyses. Only a portion of the total number of samples need to have the additional testing.

The final factor to be considered in the selection of the treatment method is economics. The three primary methods of bioremediation vary greatly in treatment time and cost. The table (p. 117) provides some criteria with which to evaluate biological treatment methods.

Land treatment (also known as *land-farming*; Figure 2) is typically the simplest and least expensive alternative. However, it requires large amounts of land that can be dedicated to the treatment process for a period of several months to several years. Typically, land treatment involves the control of oxygen, nutrients and moisture (to optimize microbial activity) while the soil is tilled or otherwise aerated.

Bioventing systems (Figures 3 and 6) are somewhat more complex at a moderate increase in cost. They are used on soils with both volatile and nonvolatile hydrocarbons. Conventional vapor extraction technology (air stripping) of the volatile components is combined with with soil conditioning (such as nutrient addition) to enhance microbial degradation. This treatment method can be utilized both in situ and ex situ. Relative to land treatment, the space requirements is reduced. Treatment time is on the order of weeks to months.

Bioreactors (Figures 1 and 4) are the most complex and expensive alternative. They can clean up contaminated water alone, or solids mixed with water (slurry bioreactors). Liquids are typically teated using fixed-film or activated-sludge processes. Slurry bioreactors are high-energy, solid-suspension systems designed to treat slurries in the 10–30% solids range. Aeration and mixing suspends the solids while the biodegradation proceeds.

The reactor can be configured from existing impoundments, aboveground tanks, or enclosed tanks (if emissions controls are required). Batch, semicontinuous or continuous modes of opera-



FIGURE 2. **Tilling with** agriculturetype equipment enhances soil aeration and speeds up land treatment





FIGURE 3. **Auxiliary skids** provide air, moisture and nutrients for an ex situ bioventing system

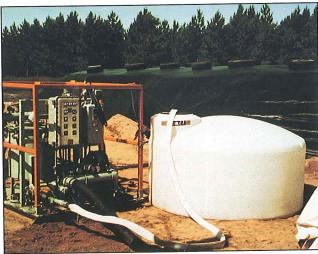


FIGURE 4. A fixed-film bioreactor, followed by an activated carbon polishing unit, takes care of contaminated groundwater at this site

OHM Corp.



FIGURE 5. This soil-washing unit serves to reduce the volume of soil needing further biotreatment

tion can be maintained. The higher cost is often justified by the faster treatment time (on the order of hours to days) as well as the ability to degrade contaminants on difficult-to-treat soil matrices.

The following examples illustrate the interaction of biological, regulatory, process engineering, and economic tradeoffs that can be encountered when selecting an appropriate method of biological treatment. Most of them are based on projects that OHM Corp. has successfully carried to completion.

## Land treatment

Biological land treatment has been used for many years in the treatment of petroleum residues. It is considered a proven treatment method for gasoline, diesel, and some crude and fuel oil constituents. The primary engineering considerations when designing a land treatment cell are bioavailability of oxvgen and nutrients, solubility of the contaminants, soil properties and the potential for migration of contaminants out of the treatment zone.

The bioavailability of oxygen (or other electron acceptors) and nutrients is essential for microbial activity. Control of these parameters in a land treatment system must consider site-specific factors and may require liners, covers, and irrigation or leachate collection systems. The solubility of the contaminant determines its availability as a carbon source for microorganisms; however, the soil may also tend to strongly adsorb the contaminant. It is difficult to improve the bioavailability of contaminants under these conditions.

OHM recently used land treatment techniques to remediate over 100,000 yd3 of petroleum hydrocarbon contaminated soil and sludge at a site in southern California. The site has three impoundments containing weathered crude oil, tars, and drilling muds ranging in concentration from 3,800 to 40,000 ppm, as measured by EPA Method 8015M. Although the hydrocarbon concentrations encountered were quite high, additional tests (flash point, pH, 96-h fish bioassay) indicated that the soil could be classified as nonhazardous.

A biotreatability study indicated that biological treatment could meet the treatment criteria (total petroleum hydrocarbons < 500 ppm). Since volatile organic compounds were not detected during the benchscale tests, emission controls were not necessary for the treatment system. Another beneficial element of the site was the availability of a large area with a low water table for construction of the treatment system.

Analysis of these factors indicated that landfarming was the most costeffective method of biological treatment. The contaminated soil was excavated and mixed with clean fill as required to reduce the liquid content of some of the sludge-like residues. The material was then placed throughout a 32-acre plot at a depth of 18 inches. This depth made the best use of the mechanical tilling equipment that turned the soil, thus ensuring adequate moisture and oxygen transfer.

An irrigation system was constructed to maintain moisture content in the optimum 10–15% range. Nitrogen and phosphorus were applied to meet nutrient requirements for the bacteria. The pH of the soil was also monitored to maintain a 7.0–7.5 range.

Following one year of treatment, contaminant levels had been reduced below the cleanup criteria of 500 ppm. Closure of the site was granted by regulators in October 1991.

#### **Bioventing**

Soil contaminated with volatile hydrocarbon compounds (for example, gasoline) can often be treated using a bioventing system. A number of factors affect the system design. For example, the oxygen demand of the microorganisms can be met by increasing airflow to the system. However, the air stream typically must be treated by vaporphase activated carbon, or thermal or catalytic oxidation, prior to discharge. This increases the size (and cost) of the emission control system. Since the treatment time may also be reduced by increasing air flow, the tradeoff of faster treatment time versus increased cost must be evaluated.

OHM recently remediated soil from a vehicle service yard contaminated with gasoline originating from an underground storage tank leak. The client was interested in treating the soil to a very low residual level so it could be

used as fill material onsite, rather than disposed offsite. Stringent air quality regulations required tight control of volatile emissions. In addition, a very limited area was available for the installation of the treatment system.

A bioventing system was recommended for this application. The process combined vapor extraction of volatile compounds and bioremediation of petroleum hydrocarbon contaminants (Figure 6). Carbon adsorbers were used to strip highly volatile gasoline components (BTX) that are also biodegradable. Biological treatment was enhanced by supplying nutrients (nitrogen and phosphorus), water, and oxygen. The rate of vapor extraction versus bioremediation was controlled by varying the air flowrate.

## Bioventing saved customers \$95/yd³, compared with disposal

A biotreatability study was not performed on this material, as experience has shown that gasoline-contaminated soil is easily remediated using indigenous bacteria. However, since the soil had a high clay content, a bulking agent was used to increase the void fraction, and thus minimize air flow channeling in the soil pile. In order to minimize the impact on the customer's operations, a modular treatment system was installed. This system was used to treat multiple lots of contaminated soil, up to a maximum size of 250 yd³/batch.

Petroleum hydrocarbon levels were reduced from 1,200 ppm to less than 10 ppm within 3 months using this method, and BTX content was nondetectable in the soil. Treatment using this method was accomplished for an average cost of \$70/yd³. Bioremediation of the contaminated soil saved the customer approximately \$95/yd³ compared to disposal at a Class 1 landfill. In addition, future liability was minimized since all material was retained onsite.

## **Bioslurry reactors**

Bioreactor treatment embodies the technical concepts that are most familiar to the chemical engineer: residence time, reaction rate, recycle ratio, Reynolds and Schmidt numbers. Bioreactors have long been used in industry for the fermentation of alcohol, for the activated sludge treatment of wastewater, and more recently, for the biological production of pharmaceuticals and industrial enzymes.

OHM was hired by a major electrical equipment manufacturer to conduct laboratory, pilot and field testing required to develop and demonstrate a bioremediation system to treat the natural degradation products of polychlorinated biphenyls (PCBs) in river sediments. This degradation produces mono-, di-, and tri-chlorobiphenyls, which are amenable to aerobic biological treatment.

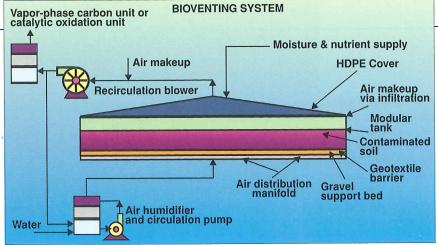
This design included six gas-tight, temperature-controlled bioreactors (each 19 feet long by 6 feet wide) that were installed into the river sediments. This allowed the bioslurry treatment process to be evaluated *in situ*. Each reactor was equipped with a mixing system of rake and turbine agitators. The reactors were mounted on a rectangular steel platform, which was supported by steel piles driven 70 ft.

The field study demonstrated that PCB-containing river sediments could be biodegraded *in situ*. The combined action of natural anaerobic dechlorination and aerobic biodegradation was shown to significantly reduce the quantity and availability of PCBs.

#### Combined systems

Remediation of sites always involves the evaluation of a diverse set of technologies. While biological treatment alone can be used for the treatment of many waste streams, combining bioremediation with other treatment technologies may provide a more cost-effective remedial alternative. The following projects are examples of these engineering and economic considerations.

Soil and groundwater treatment — A large forest-products manufacturer asked our company to remediate a site contaminated with pentachlorophenol (PCP), creosote, and other wood-treating chemicals. The site contained con-



taminated groundwater, soil and sludges. After lab studies, a two-bio-reactor system was selected, with a fixed-film bioreactor for aqueous media and slurry bioreactor for soils.

In the fixed-film bioreactor, biomass growth is attached to support media. Contaminated water flows across the media and organic contaminants are adsorbed onto and degraded in this biological layer. Conditions in the water are optimized by pH adjustment and nutrient addition. Tests run at a 5-h hydraulic residence time demonstrated 90% reduction of PCP and 70% reduction of total organic carbon (TOC).

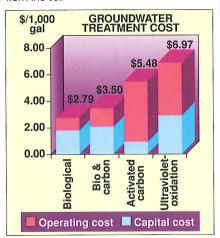
Capital and operating cost estimates were developed for pilot and fullscale aqueous treatment units. In addition, three physical-chemical treatment options were evaluated: treatment in an aqueous bioreactor followed by carbon polishing; adsorption on liquid-phase granular activated carbon; and ultraviolet-catalyzed oxidation.

The choice of alternative treatment technologies was based on two factors. Biological treatment followed by activated carbon polishing may be required in order to meet governmental discharge requirements. Liquid-phase activated carbon, and UV-oxidation are well established treatment methods for contaminated groundwater.

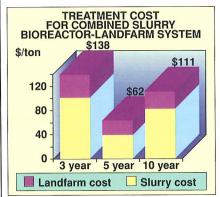
Figure 7 shows the costs for a full-scale system treating 120 gal/min. The capital cost (prorated for the life of the project) for the biological unit is twice that of the activated carbon system. However, the lower operating cost results in a total treatment cost that is half the price of its closest competitor. Carbon polishing adds 13% to the base cost.

Soils and sludges are treated using a bioslurry reactor. The contaminated material is slurried with water and placed into a mixed, aerated biotreatment unit where suspended bacteria

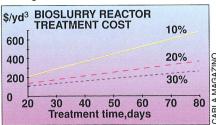
**Figure 6.** Pipes blowing air from the bottom of this enclosure separate contaminants from the soil



**Figure 7.** Under the right circumstances, biological treatment can be the lowest-cost option for groundwater cleanup



**Figure 8.** The treatment cost for this system reaches a minimum value after 5 years, then rises again



**Figure 9.** Within the operating rates of bioslurry reactors, a higher solids percentage in the feed stream reduces treatment costs

degrade the contaminants. Transfer of organic material to the aqueous phase is enhanced by pH adjustment or the addition of surfactants. Tests showed that desorption of the organic contaminants from the soil is the limiting step in the degradation process. As the contaminants partitioned into the aqueous phase, they were degraded nearly immediately by organisms in the slurry.

Observation of the short-term degradation of PCP in the initial tests suggested that a majority of the degradation occurred in the first 10 to 30 days of treatment. The extent of degradation of other aromatics ranged over 40–99% during the incubation period. These results suggested that treatment costs could be minimized by initial processing of soils in the slurry bioreactor followed by final treatment in an engineered landfarm.

Treatment costs for a bioslurry reactor system using a 30-d batch time, followed by land treatment, are given in Figure 8. The minimum cost (\$111/ton) occurs with a 5-yr remediation lifetime. An equivalent system using only the bioreactor would require a cycle time of 80+d to reach the cleanup criteria. The treatment cost can be reduced by over \$45/ton using the hybrid system.

Soil washing-bioslurrying — OHM is presently conducting a fullscale remediation of creosote-contaminated soil at the Southeastern Wood Preserving site (Canton, Miss.). A combined soil-washing and bioslurry-reactor process is being used to treat the contaminated material. Approximately 10,000 yd3 of contaminated soil is being treated in two 200,000-gal bioslurry reactors. The contaminated media consists of high-clay-content soils that were partially stabilized with kiln dust during an earlier emergency-response action. The soil contains creosote and polynuclear aromatic hydrocarbons at levels exceeding 10,000 ppm.

Figure 9 shows the general relationship between batch treatment time, solids content of the slurry, and treatment cost. For example, by increasing the solids concentration in the slurry, the throughput of the system can be increased, thus reducing the treatment cost. However, increasing the concentration of solids in the bioreactor af-

fects the rheological properties of the slurry, resulting in a decrease in oxygen transfer to the liquid phase. High solids content also introduces the possibility of inhibiting microbial growth due to to increased contaminant levels.

Oxygen limitations may result in a decline in reaction rate, and an increase in treatment cost due to longer batch times. Increasing air flow to the reactor compensates for the reduced oxygentransfer efficiency, but can cause material handling problems due to generation of large quantities of foam.

Temperature also affects the kinetics of the process. Polynuclear-aromatic degradation increases about fivefold from 15 to 40°C. In an unheated system, the reaction rate (and treatment cost) varies during the course of a year. Depending on the location of the site, the treatment process may not be able to meet the targets for contaminant reduction and treatment cost during winter months. The processing rate for the soil washing section is on the order of tons per hour; the processing rate for the slurry bioreactor is on the order of tons per day. Therefore, it is advantageous to remove as much material as practical with the soil washing step.

Following soil washing, the fine fraction containing the majority of the contamination is adjusted to make a 25%solids slurry. A microbial inoculum is then added. The inoculum consists of indigenous organisms that have been isolated from the site, and cultured onsite in a 10,000-gal breeder reactor. The slurry is then transferred into the bioreactor. The bioreactor is composed of two aerated tanks that contain the slurry. Air and a mechanical agitator are used to keep the solids in suspension. Nutrient levels, temperature, pH and dissolved oxygen are monitored and adjusted as necessary to maintain optimal conditions for microbial degradation.

From the bioreactor, material is transferred to a plastic-lined cell. Excess water is collected from the slurry via a leachate collection system. Water is decanted from the leachate collection system into a 350,000-gal tank for reuse in soil washing and slurrying operations. This design minimizes the volume of liquids that must be disposed to a public treatment works.

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Mr. Exner obtained a Ph.D. degree in physical organic chemistry from the University of Washington in 1967, and a B.S. from the University of Minnesota in 1963. He has lectured extensively on hazardous waste issues for the U.S. EPA and the American Chemical Soc. has edited three books American Chemical Soc., has edited three books on waste treatment, and published over 30 technical papers.

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