

7.0 EX-SITU BIODEGRADATION

7.1 Process Description

Ex-situ biodegradation is the general term for treatment processes in which the contaminated soil or sludge is excavated and remediated through biological processes. *Ex-situ* bioremediation technology most often involves slurry-phase bioremediation where an aqueous slurry is created by combining contaminated soil or sludge with water and then the contaminants are biodegraded in a self-contained reactor or in a lined lagoon. *Ex-situ* biodegradation also encompasses solid-phase bioremediation, such as landfarming, composting, and biopiles. In these processes, the contaminated soil is excavated, and oxygen, nutrients, water, or microorganisms are added to enhance the natural biodegradation of the contaminants.

7.1.1 Slurry-Phase Bioremediation

There are two main objectives behind using slurry-phase bioremediation: to destroy the organic contaminants in the soil or sludge, and, equally important, to reduce the volume of contaminated material. This process can be the sole treatment technology in a complete cleanup system, or it can be used in conjunction with other biological, chemical and physical treatment. Slurry biodegradation has been shown to be effective in treating highly contaminated soils that have fuel or other organic contaminant concentrations ranging from 2,500 mg/kg to 250,000 mg/kg. The slurry process has also shown potential for treating a wide range of contaminants including pesticides, creosote, pentachlorophenol, PCBs, and other halogenated organics. The effectiveness of slurry biodegradation for

certain general contaminant groups is shown in Table 7-1.

Figure 7-1 shows a general schematic of the slurry biodegradation process. However, the design of slurry processes may vary significantly among vendors. Furthermore, each vendor's process may be capable of treating only certain types of contaminants. Treatability studies to determine the biodegradability of the contaminants and the solids/liquid separation that occurs at the end of the process typically are necessary before final selection of *ex-situ* biodegradation as a remedy for a given site.

As shown in Figure 7-1, waste preparation is required before applying slurry biodegradation. The preparation may include excavation and handling of the waste material as well as screening to remove debris and large objects. Particle size reduction, water addition, and pH and temperature adjustment also may be required to meet feed specifications. Table 7-2 shows the desired feed characteristics for a typical slurry biodegradation process.

After appropriate pretreatment, the wastes are suspended in a slurry form and mixed in a tank to maximize the contact between contaminants and microorganisms capable of degrading those contaminants. From the mix tank, the slurry is pumped (using special slurry pumps) to the bioreactor system. The bioreactor system can either be an above-ground continuously stirred tank reactor (CSTR) or a lined lagoon. Since aerobic treatment is the most common mode of operation for slurry biodegradation, aeration must be provided to the bioreactors by either floating or submerged aerators or by compressors or

Table 7-1
Applicability of Slurry Biodegradation for Treatment of
Contaminants in Soil, Sediments, and Sludges

Contaminant	Applicability
ORGANIC CONTAMINANTS:	
Halogenated volatiles	1
Halogenated semivolatiles	2
Nonhalogenated volatiles	1
Nonhalogenated semivolatiles	2
PCBs	1
Pesticides	2
Dioxins/Furans	0
Organic Cyanides	1
Organic Corrosives	0
INORGANIC CONTAMINANTS:	
Volatile metals	0
Nonvolatile metals	0
Asbestos	0
Radioactive materials	0
Inorganic corrosives	0
Inorganic cyanides	1
REACTIVE CONTAMINANTS:	
Oxidizers	0
Reducers	0

Source: U.S. EPA, 1990.

KEY:

- 2 = Demonstrated Effectiveness; Successful treatability test at some scale has been completed.
- 1 = Potential Effectiveness; Expert opinion is that the technology will work.
- 0 = No Expected Effectiveness; Expert Opinion is that the technology will not work.

Figure 7-1. Slurry Bioremediation Process Flow Diagram

Table 7-2
Desired Inlet Feed Characteristics for Slurry Biodegradation Processes

Characteristic	Desired Range
Organic Content	0.025 - 25 wt %
Solid Content	10 - 40 wt %
Water Content	60 - 90 wt %
Solids Particle Size	< 1/4 in. diameter
Feed Temperature	15 -35 deg C
Feed pH	4.5 - 8.8

pargers. Nutrients and neutralizing agents also are supplied to remove any chemical limitations for microbial activity. Other materials, such as surfactants and dispersants, may be used to improve the material's handling characteristics.

In the bioreactor, microorganisms may be added initially to seed the reaction, or they may be added continuously to maintain the correct concentration of biomass. The required residence time for the waste in the bioreactor will depend on a number of factors including:

- The physical and chemical properties of the soil or sludge matrix;
- The physical and chemical properties of the contaminant, including its concentration in the waste; and
- The biodegradability of the contaminants.

A typical residence time may be as short as several days (e.g., 10) or as long as 8 to 9 weeks, depending on-site conditions.

Once the biodegradation of the contaminants is completed, the treated slurry is sent to a separation/dewatering system. A clarifier for gravity separation can be used to remove the water from the soil.

Slurry bioreactors are generally transportable units that can be brought on-site by trailer. Typically, commercial units require a set-up area of 0.5 to 1 acre per million gallons of reactor volume. Water needs at the site can be high since the waste must be put in slurry form. Large quantities of wastewater also may have to be stored on-site prior to discharge to allow time for

analytical tests to verify that the discharge standard for the site has been met.

Limited performance data on slurry biodegradation systems are currently available. Some of the data presented in this report are based on information supplied by vendors. The validity of these results has not been evaluated.

Table 7-3 shows performance data for a full-scale slurry biodegradation system designed by Remediation Technologies, which was used to treat wood preserving sludges at a site in Sweetwater, Tennessee (U.S. EPA, 1990). The system achieved an overall removal efficiency of greater than 95%, but the breakdown of the removal efficiency between biodegradation and volatilization is not available.

Another full-scale test of a slurry biodegradation system was conducted by ECOVA Corporation (U.S. EPA, 1990). In this cleanup effort, more than 750 yd³ of soil contaminated with pesticides was treated. Soil pesticide levels were reduced from 800 mg/kg to less than 20 mg/kg (>97.5% efficiency) in 13 days using a 26,000-gallon bioreactor. Residuals of the process were treated further by land application.

Under the Superfund Innovative Technology Evaluation (SITE) program, a pilot-scale demonstration of slurry-phase bioremediation was performed for creosote-contaminated soil. During a 12-week test, greater than 87% of the total polynuclear aromatic hydrocarbons (PAHs) were removed from the contaminated soil (U.S. EPA, 1993). Other case studies evaluated in the SITE report showed similar removal efficiencies. The slurry bioremediation of petroleum sludge from an impoundment

Table 7-3
Performance Results for Slurry Biodegradation Process
Treating Wood Preserving Wastes^(a)

Compound	Initial Concentration		Final Concentration		Removal ^(b)	
	Solids (mg/kg)	Slurry (mg/kg)	Solids (mg/kg)	Slurry (mg/kg)	Solids (%)	Slurry (%)
Phenol	14.6	1.4	0.7	< 0.1	95.2	92.8
Pentachlorophenol	687	64	12.3	0.8	98.2	92.8
Naphthalene	3,670	343	23	1.6	99.3	99.5
Phenanthrene & Anthracene	30,700	2,870	200	13.7	99.3	99.5
Fluoranthene	5,470	511	67	4.6	98.8	99.1
Carbazole	1,490	139	4.9	0.3	99.7	99.8

- (a) Treatment done using a 50,000 gallon reactor supplied by Remediation Technologies.
(b) Includes the combined effect of volatilization and biodegradation

yielded >90% removal of PAHs by both volatilization and biodegradation processes. Another study performed at a waste disposal services site in Texas resulted in 80% removal of most contaminants and 100% removal of some contaminants (U.S. EPA, 1993).

7.1.2 Solid-Phase Bioremediation

Solid-phase bioremediation involves the excavation and preparation of contaminated soil to enhance the bioremediation of contaminants in the soil. Land treatment (land farming) refers to the placement of the soil in an above-ground treatment system and tilling the soil at regular intervals to improve aeration and contact between the microorganisms and the contaminants. Nutrients and microorganisms may be added to the soil.

Composting involves the storage of biodegradable waste with a bulking agent to increase the porosity of the soil material. Oxygen is supplied through tilling or forced aeration. The moisture, temperature, and nutrients may need to be amended to successfully biodegrade the contaminants. Soil heap (or biopile) bioremediation is similar to composting in that the contaminated soil is piled in large mounds. However, for these processes air is usually provided by pulling a vacuum through the pile.

Table 7-4 gives a summary of the performance data available for biopile processes. Generally, the removal efficiencies of biopiles are similar to that of slurry-phase bioremediation systems. At the McClellan AFB site, both a biopile and a slurry phase process were tested. The removal efficiencies were 76% and 88%, respectively (Stefanoff and Garcia, 1995).

7.2 Identification of Air Emission Points

As shown in Figure 7-1, there are three primary waste streams generated in slurry-phase bioremediation processes: the treated solids (sludge or soil), the process water, and air emissions. The solids are dewatered and may be further treated if they still contain organic contaminants. Also, if the solids are contaminated with inorganics or heavy metals, they can be stabilized before disposal. Some portion of the process water can be recycled, with the remainder treated in an on-site treatment system prior to discharge.

The air emissions from slurry biodegradation processes can either be area or point sources. For processes using open lagoons, emissions come from the exposed surface of the lagoon. In systems using above-ground self-contained reactors, the primary source of emissions usually is a process vent. The air emissions from composting and land treatment systems usually are area emissions, whereas the emissions from biopiles can be area or point sources depending on the air delivery system.

7.3 Typical Air Emission Species of Concern

In *ex-situ* bioremediation processes, the emissions of concern are usually VOCs. The soils-handling steps required to deliver the contaminated soil to the treatment unit may also emit significant amounts of PM. Emissions from soils handling are addressed in Section 3 of this document.

Table 7-4
Summary of Performance Data for Biopile Systems

Site	Contaminants	Initial Contaminant Concentration	TPH Removal	Notes	Reference
Distribution facility in Tustin, CA	Gasoline	85 to 8900 ppm TPH; average = 1296 ppm	TPH below action levels (50 ppm) in 100% of the treated soil	80 days remediation	Autry and Ellis, 1992
Unknown	Petroleum	1100 to 3300 mg/kg TPH; average = 1187 mg/kg	>90%	Typical final concentration: 48 mg/kg	Hater et al., 1994
Refinery	Refined products and crude oil	NA	55%	Contamination is very weathered	Hayes et al., 1995
McClellan AFB, CA	Fuel and oil disposal site	3900 mg/kg TPH	76%	Final concentration: 920 mg/kg	Stefanoff and Garcia, 1995
Glass bottle manufacturing facility	Fuel oil	Up to 20,000 mg/kg TPH	90% HC 100% gasoline components	Off-gas recirculated through soil pile	Miller 1995

7.4 Summary of Air Emissions Data

Little information exists on volatile losses from *ex-situ* bioremediation processes. Table 7-5 summarizes the data available for both slurry-phase and biopile systems. Although these data are limited, volatilization appears to be a small component of the overall removal of hydrocarbons in these processes.

In open lagoons and composting and land treatment processes, the primary environmental factors which influence air emissions, in addition to the biodegradability and volatility of the waste, are process temperature and wind speed. Emissions tend to increase with an increase in surface turbulence due to wind or mechanical agitation. Temperature affects emissions through its influence on microbial growth. At temperatures outside the band for optimal microbial activity, volatilization will increase (U.S. EPA, 1989a). Emissions from self-contained reactors are also determined by reactor design parameters such as the amount of air or oxygen used to aerate the slurry. Higher gas flow will strip more volatiles out of solution and increase air emissions.

7.5 Air Emissions Controls

When the air emissions from slurry biodegradation or biopiles processes are released through a process vent, standard VOC air pollution control technologies can be applied. Common alternatives for controlling VOC vent emissions include carbon adsorption as well as thermal and catalytic oxidation. The vent stream will likely contain dilute amounts of VOCs, so auxiliary fuel must be used in either thermal or catalytic oxidizers. For the relatively low VOC levels and low gas flows from

bioreactors and biopiles, carbon-based VOC emission controls are generally the best choice for point source emissions. For biopiles, the off-gas stream can be recirculated to the heap to reduce VOC emissions further through biodegradation.

When the air emissions from *ex-situ* bioremediation processes are area emission sources, applying air pollution control technologies is more difficult. Two control options are commonly used. The first alternative is to use a vapor collection hood to capture any VOC emissions and then route those emissions to a standard control device. A second, generally less favorable, alternative is to use an oil film or foam on top of the slurry to suppress evaporative losses. Typically, the air emissions from area sources are small and do not require controls.

7.6 Costs for Remediation

Presently there are little cost data available on slurry biodegradation processes because of limited experience with this type of remediation. The cost for slurry-phase bioremediation is estimated at \$50 to \$250/yd³ (U.S. EPA, 1993). One vendor estimates the cost of full-scale operation to be \$85-160/yd³ of soil, depending on the initial contaminant concentration and the total amount of soil to be treated. The process cost will also vary depending on the need for additional pre- and post-treatment of the soil and on the type of air emissions control equipment. Labor costs for materials handling and operation can account for one-half of the cost of these systems (U.S. EPA, 1993).

**Table 7-5
Summary of Emissions Data for Ex-Situ Bioremediation Systems**

Site	Contaminants	Emission Rate	Total Emissions	Biodegradation/ Volatilization	Notes	Reference
Slurry-phase bioremediation						
Burlington Northern Superfund site, MN	Creosote	0.014 lb/hr THC max (day 1); 0.00015 lb/hr THC (day 6)	NA	NA	Off-gas concentrations peaked during day 1 and decreased to near baseline by day 5.	U.S. EPA, 1991
Refinery	Petroleum sludge	NA	910 kg HC	NA	425,000 kg of soils were treated. Emissions reduced to background by day 6.	U.S. EPA, 1993
Sheridan disposal services site, TX	Petroleum sludge	NA	10-20 kg/yr; 1.5 kg dredging 30 kg storage tank; 4 kg pond	NA	A full-scale system is estimated to have 500 to 2,000 kg of VOC emissions.	U.S. EPA, 1993

**Table 7-5
(Continued)**

Site	Contaminants	Emission Rate	Total Emissions	Biodegradation/ Volatilization	Notes	Reference
Biopile						
Distribution facility in Tustin, CA	Gasoline	NA	NA	99%/1%	Air emissions measured for the stockpiling/handling, mixing, and curing operations. Mixing component accounted for 96% of contaminants lost. 73% of VOCs lost were trapped in carbon units.	Autry and Ellis, 1992
Unknown	Petroleum	0.021 lb/hr HC once through; 0.067 lb/hr HC after treatment (carbon)	NA	NA	Off-gas was also recycled back to the biopiles to further reduce emissions.	Hater et al., 1994
Refinery	Petroleum	16 ppb BTEX startup; 5 ppb BTEX (day 8); <1 ppb BTEX (day 35)	NA	>99%/<1%		Hayes et al., 1995

The cost of biopiles and other solid-phase bioremediation processes are less known. One study found that a biopile was more cost-effective than a slurry-phase system because the biopile was more robust with respect to varying soil characteristics and because of the difficulties in dewatering slurries (Stefanoff and Garcia, 1995).

The materials handling component is consistent across all types of *ex-situ* bioremediation processes, so most of the cost differences would occur in the treatment and post-treatment portions of these processes.

7.7 Costs for Emissions Controls

Equations for predicting the costs of emission controls based on system design parameters are available (PRE, 1989). Section 5 of this document provides typical costs for various types and sizes of treatment systems which could be applied to an *ex-situ* biodegradation process. As mentioned in Section 5, the cost estimates are drawn from a number of vendors and, therefore, a range is shown in most cases. The cost data are intended to show the general level of costs likely to be incurred.

7.8 Equations and Models for Estimating Air Emissions

Although no models have been explicitly developed for estimating emissions from *ex-situ* bioprocesses used to treat contaminated soil, there are currently, several public-domain PC models available for estimating air emissions from a variety of other biotreatment options, principally surface impoundments. The two most commonly used models are CHEMDAT-7 (U.S. EPA, 1989b) and the Surface Impoundment Modeling System (SIMS).

Both CHEMDAT-7 and SIMS are based on mass transfer and biodegradation models developed by the U.S. EPA. The mass transfer model uses two-film resistance theory, along with the characteristics of the impoundment, to estimate overall mass transfer coefficients for each pollutant. The biodegradation model assumes Monod kinetics to estimate a biodegradation rate.

The accuracy of estimating emissions from *ex-situ* biotreatment processes, though, is limited by the assumptions inherent in both CHEMDAT-7 and SIMS. Both models perform all calculations at 25°C and rely on physical property and kinetic data that are not always readily available for the modeled contaminants. Furthermore, both models rely on a simple thermodynamic analysis and are only valid in the Henry's Law regime. Henry's Law is applicable to dilute solutions and may not be applicable to bioslurries. In addition, neither CHEMDAT-7 nor SIMS use thermodynamic models that can predict the presence of two liquid phases.

The validity of CHEMDAT-7 and SIMS for modeling emissions from *ex-situ* biotreatment processes will depend on the process used and the operating parameters. Their validity must be evaluated on a case-by-case basis. If these models prove to be unacceptable for a given application, emissions can be estimated using a simple mass balance approach. For continuous-flow slurry systems, the following simple correlation is applicable (Thompson, et al., 1991):

$$ER_i = (C_i/1,000)(M_i)(V_i/100)$$

where:

ER_i = emission rate for contaminant i (g/hr);

C_i = concentration of species i in contaminated soil (mg/kg);

M_r = mass rate of soil treated (kg/hr); and

V_i = percentage of contaminant i volatilized (%).

The percentage of each contaminant that is volatilized will vary greatly depending on the physical properties of the contaminant and the design of the treatment system.

Based on field studies of an aerated impoundment treating contaminated water, as much as 20% of each compound may be volatilized depending on its volatility and biodegradability (Eklund, et al. 1988).

For batch slurry biotreatment systems, a similar expression can be used to estimate air emissions:

$$ER_i = (C_i/1,000)(M)(\% V_i/100)/(t)$$

where:

ER_i = emission rate for contaminant i (g/hr);

C_i = concentration of species i in contaminated soil (mg/kg);

M = mass of soil treated (kg);

V_i = percentage of contaminant i volatilized (%); and

t = residence time in treatment system.

Again, volatilization may be 20% or higher, depending on the properties of the compound of interest. This equation can also be used to estimate the emissions from solid-phase bioremediation processes.

Emissions will also occur when excavating the contaminated soil, while transporting it to the treatment unit, during any soil preparation steps, and when feeding the soil into the treatment process. These fugitive emissions are not addressed in either the PC-based models or in the mass balance equations discussed above. Fugitive VOC emissions from soils handling operations are addressed in Section 3.

7.9 Case Study

No suitable case study was found for the *ex-situ* bioremediation of soils contaminated with petroleum hydrocarbons.

7.10 References

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