United States
Environmental Protection
Agency
Research and Development

Hazardous Waste Engineering
Research Laboratory
Cincinnati OH 45268

EPA/540/S2-86/002 Mar. 1987

EPA

Project Summary

Systems to Accelerate In Situ Stabilization of Waste Deposits

In situ systems to accelerate the stabilization of waste deposits have been presented as alternatives to containment, isolation or excavation as methods for remediation of uncontrolled waste sites. In situ applications involve three essential elements: selection of a chemical or biological agent (reactant) which can react with and stabilize the waste, a method for delivery of the reactant to the deposit and a method for recovery of the reaction products or mobilized waste. The most promising applications for in situ treatment methods are for spill or plume types of contamination, where the contaminants are relatively evenly distributed and preferably in liquid form. Delivery of reactants to solid, heterogeneous, low permeability deposits will be more difficult. In situ methods may find particular application when used in combination with other remedial measures, for example, removal of the source material and in situ treatment of the plume.

Four reactant categories have been examined: biodegradation, surfactant-assistant flushing, hydrolysis, and oxidation. Of these, biodegradation and surfactant-assisted flushing appear most promising as in situ treatment techniques. For any treatment technique, the potential toxicity of the applied reactant and any intermediate compounds or by-products must be carefully evaluated. Furthermore, the potential for undesirable reactions with other contaminants present must be studied (e.g., oxidation of phenol with hydrogen peroxide may also oxidize chromium (III) to the more toxic hexavalent chromium).

Methods of delivery of reactants based upon gravity include surface flooding, ponding, surface spraying, ditching, and subsurface infiltration beds and galleries. Forced injection (pumping) may also be used. Permeability is an important consideration in selecting the delivery system. Gravity delivery methods require a permeability of the soil/waste medium in the range 10^{-1} cm/sec to 10^{-3} cm/sec (280 to 2.8 ft/day). Forced injection is most effective at a permeability in the range of 10^{-1} cm/sec to 10^{-4} cm/sec (280 to 0.28 ft/day); below this permeability limit a potential application of forced injection for reagent delivery coupled with electro-osmosis for recovery may exist. Additionally, gravity systems should be considered only when the waste deposit lies in the unsaturated zone and when the depth to the bottom of the deposit is less than 5 meters (16 feet). Otherwise, forced injection should be considered.

Recovery systems using gravity include open ditching and buried drains, and pumped methods include wellpoint and deep well systems. Basically, the same limitations that apply to delivery systems are also true for recovery systems. Gravity-induced recovery works best when the water table is wrnin 5 meters (16 ft) of the surface. For depths in the range of 0-8 meters (0-26 ft), well points can also be considered. Depths greater than the suction limit (about 8 meters or 26 ft in practice) will require the use of down-hole pumps for recovery.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This project represents Phase I of a two phase scope of work to document the feasibility of engineered approaches to treating subsurface waste deposits through the application of in situ methods. Phase I concentrated on applications of available technology and examined the limitations imposed on their use by site and waste specific characteristics. A future phase of the project, Phase II, is expected to undertake bench scale or pilot studies to expand the data base available to potential users of in situ methods.

Procedure

The six part program of investigation consisted of a literature review, a definition of the capabilities and limitations of delivery, recovery and treatment technologies, visits to sites where remedial activities were underway, a definition of important site and waste characteristics, and an evaluation of remedial technologies. The available data were evaluated to determine classes of organic chemicals amenable to treatment by various potential in situ treatment methods. Potential delivery and recovery systems for these treatment agents were then evaluated with respect to site hydrogeologic characteristics. The guidance manual which was developed identifies combinations of delivery/recovery technologies and reagents that have a reasonably high or clearly low probability of success for in situ treatment of hazardous waste.

Results and Discussion

Systems to accelerate stabilization of waste deposits will require (1) selection of delivery/recovery methods for the treatment technology compatible with site characteristics and the waste deposit setting, and (2) selection of a suitable treatment technology that will be compatible with waste composition and site characteristics.

Delivery/Recovery Systems

The selection of the most appropriate delivery/recovery methods and systems requires a thorough understanding of the waste deposit site characteristics. The site must be defined with respect to the configuration of the waste deposit (areal extent and vertical depth), hydrologic characteristics (surface and subsurface) of the waste deposit, and surface and subsurface geohydrologic characteristics of the materials surrounding the waste deposit.

Delivery Methods

The matrix for selection of delivery methods is presented in Table 1. The table shows the forced delivery method is applicable for all conditions. The choice of a gravity delivery method is more dependent on the listed parameters. The listed parameters indicate differences in site characteristics that would warrant selection of one delivery method(s) over the others. These parameters were selected for the following reasons:

- Average Permeability of the Waste Deposit.
  Permeability will dictate the flow characteristics of the deposit. If the permeability of the deposit is high, then low net pressure and short time durations would be required for a solution to pass through the deposit. Low permeability means the deposit is not easily drainable and would require higher pressure and longer time duration for a solution to move through the deposit. Gravity methods are most effective for highly permeable waste deposits.
- Depth to the Waste Deposit.
  Engineering judgement is the basis for selecting between gravity and forced delivery methods at each specific site. If the depth is too great, then gravity delivery will lengthen the time for a solution to travel to the deposit, or extensive excavation may be required to obtain effective gravity delivery. A reasonable maximum depth for gravity delivery is judged to be about 5 meters (15 feet).
- Waste Deposit Covered by an Impermeable Layer.
  For the forced delivery method this parameter has no bearing, although for gravity delivery methods it will have a significant impact. For example, flooding and spray irrigation cannot be utilized as delivery methods if the surface of the deposit is topped by an impermeable layer of soil or synthetic material.
- Topography.
  Topographic considerations will limit, in part, the extent of applicability of gravity flow methods. For example, on a steep slope flooding or ponding delivery methods cannot be utilized. However, topograhpy will not affect the forced delivery methods(s).
- Infiltration Rate.
  Gravity delivery at the deposit surface is most effective for deposits with high infiltration rates. Infiltration rate has no bearing in forced delivery systems.
  In general, gravity delivery methods are effective when the waste deposit is situated in the unsaturated zone with shallow permeable overburden, and depth to the deposit is limited to 15 feet with permeability greater than 10^{-3} cm/sec.
  For waste deposits covered by thick overburdens of significant depth (more than 5 meters) the forced delivery method will be most effective. For waste deposits having a permeab lower than 10^{-4} cm/sec a forced method utilizing electro-osmosis could be employed for solution injection into the deposit. In general, the forced method should be highly effective for waste deposits within a permeability range of 10^{-1} cm/sec to 10^{-4} cm/sec.

Recovery Methods

Table 2 indicates the applicability of various recovery methods for different site characteristics. Only two parameters, depth to recovery zone and composite permeability, are considered in the matrix. Although other parameters such as transmission and storage may play an important role in designing well or well point systems, these two parameters are the most appropriate guide for the preliminary selection of recovery methods. It should be noted that the recovery of injected solution will be from the saturated zone (water table aquifer) and normally the recovery method(s) will be installed beyond the boundary of the waste deposit. However, when a recovery method is installed within the waste deposit, the composite permeability of the waste deposit should be considered in selecting the recovery method. The parameter, depth to recovery zone, is chosen because gravity methods are practical beyond a 5 meter depth ' vacuum well points are also effective to a 5 to 8 meter depth. The permeability will dictate the drainage characteristics and thereby control the selection of recovery (dewatering) methods.

In general, gravity recovery methods are suitable for a shallow recovery zone (depth to water table from the surface should not be more than 5 meters). For a deeper recovery zone, forced recovery methods must be employed.

The two basic treatment concepts evaluated are in situ waste destruction by biodegradation, hydrolysis or chemical oxidation, and surfactant-assisted flushing to mobilize the contaminants and facilitate further in situ treatment or recovery followed by above-ground treatment. Potential applications of these methods to various classes of organic contaminants are presented in Table 3.

Biological Renovation of Waste Deposits

Aerobic and anaerobic bacteria, fungi, actinomycetes, algae and cyanophytes (blue-green algae) have all been shown capable of degrading many classes of organic chemicals. These microbes include natural microbial populations, ada microbial cultures and potentially bi

Table 1. *Matrix for Delivery Methods*

Delivery Methods	Location of the deposit in relation to existing groundwater table			Contamination starts at		Thickness of overlying impermeable layer			Topography (Slope)			Infiltration Rate cm/hr (inches/hr)			Hydraulic Conductivity cm/sec (ft/day)			Depth to Bottom of the Waste Deposit Meters (ft)		
	Unsaturated	Partially Saturated	Saturated	Surface	Subsurface	0	<1.5m (>5 ft)	>1.5m (>5 ft)	Flat	0-3%	>3%	.1–.2 (.3–5)	.06–.1 (.15–.3)	<06 <0.15	$10^{-1}-10^{-3}$ (280–2.8)	$10^{-3}-10^{-4}$ (2.8–0.28)	$10^{-4}-10^{-7}$ (0.28–0.0003)	<5 (<16)	5–12 (16-40)	>12 (>40)
GRAVITY																				
1. Flooding	X	LE	NA	X	X	X	NA	NA	X	X	NA	X	X	NA	LE	NA	NA	X	LE	NA
2. Ponding	X	LE	NA	X	X	X	X	NA	X	X	NA	X	X	LE	X	LE	NA	X	LE	NA
3. Surface Spraying	X	NA	NA	X	X	X	NA	NA	X	X	LE	X	X	NA	LE	NA	NA	X	LE	NA
4. Ditches	X	LE	NA	NA	X	X	X	NA	X	X	X	X	X	X	X	LE	NA	X	LE	NA
5. Infiltration Galleries	X	LE	NA	NA	X	X	X	X	X	X	X	X	X	X	X	LE	NA	X	X	NA
6. Infiltration Bed	X	LE	NA	NA	X	X	X	X	X	X	NA	X	X	X	X	LE	NA	X	X	NA
FORCED																				
1. Injection Pipes	X	X	X	X(1)	X	X	X	X	X	X	X	X	X	X	X	X	X(2)	X	X	X

X = Applicable
LE = Less Effective
NA = Not Applicable
(1) = May need combined gravity and forced delivery.
(2) = Applicable with electro-osmosis.

Table 2. *Matrix for Recovery Methods*

Recovery Methods	Depth To Groundwater			Hydraulic Conductivity		
	0–5 m (0–16 ft)	5–12m (16–40 ft)	>12 m (>40 ft)	$>10^{-1}-10^{-3}$ cm/sec (>280–2.8 ft/day)	$10^{-3}-10^{-4}$ cm/sec (2.8–0.28 ft/day)	$10^{-4}-10^{-7}$ cm/sec (0.28–0.003 ft/day)
GRAVITY:						
Open Ditches and Trenches	X	NA	NA	X	LE	NA
Porous Drains	X	NA	NA	X	LE	NA
FORCED:						
Wellpoint	X	X	NA	X	LE	NA
Deep Well	NA	X	X	X	LE	NA
Vacuum Well Point	X	X	NA	NA	X	LE
Electro-osmosis	X	X	X	NA	NA	X

X = Applicable
LE = Less Effective
NA = Not Applicable

gineered microbial strains. Once the extent of the contamination and its chemical characterization have been determined, the proper microorganisms (or groups of microbes) may be identified and developed. The identification of the proper agents for waste site renovation is based upon past experience, laboratory screening, and onsite pilot-scale tests.

To date, aerobic bacteria such as pseudomonas have been most commonly used for in situ biodegradation of contaminants. These organisms can potentially completely convert the organic compounds to CO_2 and water, and do not produce H_2S or methane as reaction products. However, anaerobic bacteria are important for the biodegradation of pesticides and halogenated organics. Organic contaminants that have been successfully treated by biodegradation include phenols, gasoline and other petroleum products, methylene chloride, alcohols and acetone.

In the process of designing the microbial waste treatment system, one must determine the oxygen, emulsifier (if the wastes are insoluble) and fertilizer requirements for optimum waste treatment rates. Microbial agents require the maintenance of sufficient concentrations of nitrogen, phosphorus and trace elements, and a pH range that will support their growth. The levels of these factors at the site should be determined during the site investigation; the need for additional fertilizers or buffers required to support microbial growth can then be identified.

Biological renovation of subsurface waste deposits poses problems relating to oxygen supply, temperature, permeability and accessibility not encountered with surface disposal sites. Injection wells may be established into and below the waste site to deliver a fertilizer and oxygen supply. Oxygen sources would include injectable solutions of peroxides, oxygen-charged water produced by ozonation, or direct sparging of air into the ground water. Recovery wells or trenches should be situated at points peripheral to or downgradient of the waste deposit. Flow patterns established between injection and recovery wells should be planned to aid in confining the waste during the renovation process. In this way ground water plumes that may be migrating from the site can be renovated as well.

Application of Hydrolysis to Waste Deposit Stabilization

Hydrolysis is a chemical reaction involving the cleavage of a molecular bond by reaction with water. The rates of hydrolysis for some compounds can be accelerated by altering the solution pH, temperature, solvent composition, or by introducing catalysts. For in situ treatment, alternation of pH, particularly raising the pH (base-catalyzed hydrolysis), is the most promising approach. The range of chemical classes potentially treated by base-catalyzed hydrolysis includes amides, esters, carbamates, organo-phosphorus

Table 3. *Potential Applications of Treatment Methods to Waste Contaminants*

Chemical Class	Bio-degradation	Hydrolysis(1)	Oxidation(2)	Water Flushing(3)	Surfactant Flushing(3)
Aliphatic Hydrocarbons	+	–	+	–	+
Alkyl Halides	+	+	?	–	?
Ethers	+	–	?	–	+?
Halogenated Ethers and Epoxides	+	+	?	?	?
Alcohols	+	–	+	+	–
Glycols/Epoxides	+	–/+	+	?	?
Aldehydes, Ketones	+	–	+	+?	–?
Carboxylic Acids	+	–	+	?	?
Amides	+	+	+	?	?
Esters	+	+	?	?	?
Nitriles	+	+	+	?	?
Amines	+	+	+	+?	–?
Azo Compounds, Hydrazine Derivatives	+	–	+	?	?
Nitrosamines	+	–	+	?	?
Thiols	+	–	+	?	?
Sulfides, Disulfides	+	–	+	?	?
Sulfonic Acids, Sulfoxides	+	?	?	?	?
Benzene & Substituted Benzene	+	–	+	–	+
Halogenated Aromatic Compounds	+	–	?	–	+
Aromatic Nitro Compounds	+	–	+	?	?
Phenols	+	–	+	+	–
Halogenated Phenolic Compounds	+	–	+	?	?
Nitrophenolic Compounds	+	–	+	?	?
Fused Polycyclic Hydrocarbons	+	–	+	–	+
Fused Non-Aromatic Polycyclics	+	–	+	–	+
Heterocyclic Nitrogen Compounds	+	–	+	–	+?
Heterocyclic Oxygen Compounds	+	–	+	–	+
Heterocyclic Sulfur Compounds	+	–	?	–	+
Organophosphorus Compounds	+	+	?	?	?
Carbamates	+	+	?	?	?
Pesticides	+	+	?	?	?

(1) *Based upon calculated half-lives for base catalyzed at pH 9 to 11.*
(2) *Based on oxidation of chemicals in water and wastewater by H_2O_2.*
(3) *Based upon aqueous solubility and octanol/water partition coefficient (K_{ow}).*
+ = *can be used* ? = *futher research needed*
– = *cannot be used* –? = *probably cannot be used*
+? = *probably can be used*

compounds, pesticides and herbicides. Base-catalyzed hydrolysis has been successfully used for treatment of surface spills of acrylonitrile and pesticides.

The primary design concern for implementation of base-catalyzed hydrolysis within a waste deposit will be the production and maintenance of high pH (9 to 11) conditions with saturation or high moisture content in the waste deposit. For shallow subsurface or surface deposits, surface application of lime, sodium carbonate or sodium hydroxide followed by surface application of water may be appropriate. For deeper deposits, subsurface delivery or injection of alkaline solutions may be required.

Potential for In Situ Oxidation of Waste Deposits

The potential application of three oxidants (ozone, hydrogen peroxide, and hypochlorites) to waste deposits was evaluated. Although in widespread use in surface water treatment applications, significant problems may preclude their effective implementation as in situ treatment agents for waste deposits.

Hypochlorite reacts with organic compounds as both a chlorinating agent and an oxidizing agent. Documentation on the effectiveness of hypochlorite as an oxidizing agent for organic materials is extremely limited. Hypochlorite additions may lead to production of undesirable chlorinated by-products (e.g., chloroform) rather than oxidative degradation products. Therefore the use of hypochlorite for in situ treatment of organic wastes is not recommended.

While ozone is an effective oxidizing agent for many organic compounds in wastewater treatment applications, its relatively rapid decomposition rates in aqueous systems, particularly in the presence of certain chemical contaminants or other agents which catalyze its decomposition to oxygen, preclude its effective application to subsurface waste deposits. The half-life of ozone in ground water is less than one-half hour. Considering that flow rates of water through waste deposits likely to be on the order of inches/hour or less, it is unlikely that effective oxidant doses of ozone can be delivered outside of the immediate vicinity of the point of application. Successful use of ozone for in situ chemical oxidation is unlikely. However, ozonation has been used successfully to supply oxygen for microbial biodegradation, and to chemically oxidize complex organics in a surface reactor to simpler compounds that are more readily biodegradable. This use of ozone as a supplementary treatment for biodegradation seems promising.

Hydrogen peroxide is a weaker ozidizing agent than ozone; however, its stability in water is considerably greater. Since decomposition of hydrogen peroxide to oxygen may be catalyzed by iron or certain other metals, effective delivery of hydrogen peroxide throughout an entire waste deposit may be difficult or impossible because of the relatively low transport velocities achievable in waste deposits. Prior to consideration of hydrogen peroxide as an in situ treatment method, it will be necessary to investigate the stability (or rate of decomposition) of hydrogen peroxide in the specific waste deposit matrix. Hydrogen peroxide may also be used as an oxygen source for microbial biodegradation.

Surfactant-Assisted Flushing or Solubilization of Wastes

Flushing or mobilization of wastes can serve two purposes: to promote the recovery of wastes from the subsurface for treatment on the surface, or to solubilize adsorbed compounds in order to enhance the rate of other in situ treatment techniques (such as biodegradation or hydrolysis). Flushing or mobilization using water alone may be sufficient for relatively soluble compounds such as phenols; however, the use of surfactants will be required for significant solubilization of insoluble (hydrophobic) compounds.

Surfactants (surface active agents) are a class of natural and synthetic chemicals which promote the wetting, solubilization, and emulsification of various types of organic chemicals. A simple approach to evaluating the potential use of surfactants in organic waste recovery involves consideration of the aqueous solubility or octanol-water partition coefficient, K_{ow}. Surfactants would be most effective in promoting the mobilization of organic compounds of relatively low water solubility and high K_{ow} values.

Laboratory tests suggest that surfactants may enhance the recovery of subsurface gasoline leaks by groundwater pumping, and promote the mobilization of crude oil and PCBs from soils. However, certain environmental factors may reduce the in situ effectiveness of surfactants. These include precipitation of the surfactant by groundwater with high TDS or alkaline earth cation concentrations (Ca, Mg); reduction of surfactant effectiveness due to nonoptimal pH or temperature; or adsorption of the surfactant by soil particles, negating its solubilizing properties. Nevertheless, the use of surfactants either alone (to flush otherwise insoluble organics) or in combination with other treatments (to solubilize the waste materials and thereby promote biodegradation) is a promising avenue for further research.

Selection and Evaluation of Systems for Treatment of Specific Waste Problems

Before final selection of delivery/recovery and treatment methods, the following steps must be undertaken for each site:

Initial Site Evaluation -

In this phase the following information is obtained for each site:

- Extent and nature of the waste deposit;
- Site soil characteristics such as porosity and permeability, and uniformity;
- Surface drainage characteristics of the site;
- Groundwater table location and groundwater flow direction and velocity;
- Field permeability testing of the waste deposit and host materials;
- Surface infiltration rate;
- Soil, waste deposit and groundwater samples collection and laboratory analyses.

Identification of Feasible Methods

Based on the field investigations and laboratory testing, feasible treatment and delivery/recovery methods commensurate with the treatment requirements, are identified using the matrices in Tables 1 through 3. These feasible methods are carefully evaluated based on engineering judgement to narrow down the choices for the field demonstration program.

Bench Scale Tests

Bench scale tests may be necessary to demonstrate the effectiveness of a given treatment method for a specific combination of chemical contaminants and waste deposit matrix.

Field Demonstration Program

A field demonstration program for the selected feasible methods is undertaken to evaluate the effectiveness of the methods and to generate design information, such as ditch spacing and well spacing required for proper delivery and recovery of the treatment agent.

Design and Economic Evaluation of the Effective Methods

Based on the field demonstration program, alternate delivery/recovery systems are developed and a cost evaluation is performed. Based on cost and effectiveness analysis, final selection of a delivery/recovery system was made for subsequent implementation.

Conclusions and Recommendations

To accelerate stabilization of waste piles or deposits using a combination of chemical or biological reagents and delivery/recovery systems involving gravity or forced methods of injection, a great deal more information based upon specific field experimentation must be assembled.

Each in situ application will resemble a research effort which must be customized to the site and waste characteristics. The essence of a successful application of an in situ method is the performance of a treatability study designed to account for the peculiarities of the waste and treatment reagent combination as well as the unique geohydrological characteristics of the site. Since treatability studies cannot exist for the generalized case, almost all conclusions to be drawn from the literature survey were necessarily based upon engineering judgement. Verification of hypotheses by reference to documented field experience was not feasible in most situations.

A major constraint on the feasibility of in situ treatment is the degree of homogeneity of the waste deposit. Subsurface deposits contained in drums or within nonuniform formations which impede the flow of waterborne reagents cannot be considered as realistic candidates for in situ treatment. The experience that exists strongly suggests that the greatest in situ success will be with a plume or a spill situation rather than with a source deposit itself.

The full report was submitted in fulfillment of Contract No. 68-03-3113, Task 37-2 by JRB Associates under the sponsorship of the U.S. Environmental Protection Agency.