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CLEANING CONTAMINATED EXCAVATED SOIL USING EXTRACTION AGENTS

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Prepared for

Enviresponse, Inc.
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Contract 68-03-3255

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INTRODUCTION

BACKGROUND

Under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the current National Contingency Plan (NCP) that implements it, response actions at hazardous waste sites must reduce the threat of controlled wastes. In the 1984 Resource Conservation and Recovery Act (RCRA) Amendment, Congress clearly showed its intent to minimize the volume of solid waste disposal in landfills. This policy would mandate a major change in the current practices at CERCLA sites of removing the hazardous waste material and burying it elsewhere.

The policy of the Office of Solid Waste and Emergency Response (OSWER), responsible for implementing the 1984 RCRA Amendments, is to discourage containment-based disposal of CERCLA waste and encourage technologies to eliminate or reduce the hazardous character of the waste. On-site treatment technologies that destroy or reduce contaminant levels achieve more positive control than containment techniques. Off-site disposal to landfills will probably be allowed in the future, but only when no destruction technology is available, because transportation of a hazardous waste creates opportunities for spills and accidents. In addition, as landfill disposal becomes more expensive and as hazardous waste transportation is more stringently regulated, on-site waste destruction technologies will become more desirable--if they are technologically demonstrated, environmentally safe, and affordable.

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ON-SITE SOIL TREATMENT

Soil contamination at NPL sites should be reduced in the near term to keep the contaminants away from the public. Containment of the contaminants by isolation does not always offer a permanent solution. Off-site treatment services are not always available or appropriate. On-site treatment to diminish the contaminant level should be considered an alternative to isolation or off-site treatment--even if the remedial cost is higher.

On-site treatment options include in-situ leaching, incineration, fixation, and cleaning of excavated soil. In-situ treatment involves techniques such as injecting grout, trenched slurry walls, steel pilings, etc., to isolate the treatment region, followed by leaching of the contaminant by soil percolation within the perimeter. The contaminated fluid is pumped from a distributed well field for above-ground treatment. Another in-situ technique is to inject fluid, at multiple intervals, to change the contaminant chemically or immobilize it. Incineration offers a second choice for excavated soil contaminated with organics. A third option is above-ground fixation of the contaminant and redeposit of the treated soil. A fourth option--above-ground soil cleaning--has been limited to research investigations. The substantial costs associated with process design and equipment development have dampened interest in the soil-cleaning technique.

The advantages and disadvantages of the four on-site technologies are presented in Table 1. In-situ leaching or fixation is the least expensive, if applicable. Incineration of organic compounds may be appropriate if the soil does not contain high concentrations of hazardous metals or inorganic

contaminants. Cleaning (washing) of excavated soils holds promise for being

applicable to all contaminants. But because it has not been successfully dem-

onstrated on a large scale in the field, further development work is needed.

TABLE 1. COMPARISON OF ON-SITE SOIL TREATMENT TECHNOLOGIES

On-Site Treatment To Reduce Hazard	Advantages	Disadvantages
In-situ leaching or fixation	● Lower cost ● Applicable to most contaminant types	● Not applicable if soil is impermeable ● Leaching may require years
Incineration	● Established technology ● Complete destruction of organics	● Not applicable to inorganics ● Some soil may be difficult to handle and foul the incinerators
Fixation	● Applicable to metals and inorganics ● Fast cleanup of site	● Not applicable to organics ● May increase the volume of the soil
Soil cleaning	● Removal of all contaminant types ● Site may be cleaned quickly	● Costly equipment ● No large-scale demonstration

SOIL CLEANING FOR SAFE ON-SITE REDEPOSIT

Soil cleaning employing extraction agents consists of soil excavation,

above-ground on-site treatment, isolation and removal or destruction of the

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contaminant, and redeposit of the cleaned soil. Each technique to separate the

contaminant from the soil requires an extraction agent--a liquid, gas, chemical

additive, heat, or a combination of agents. The agent must forcefully mobilize

the contaminant, which is chemically or physically attached to the soil par-

ticles.

SECTION 2

PATTERNS OF CONTAMINATION AND SOIL COMPOSITION AT NPL SITES

An understanding of the frequency of occurrence of the possible soil type/soil contaminant pairs can guide the selection of agents or processes for further investigation and development.

CLASSIFICATION OF CONTAMINANTS

The most common multicompound concentration analyses performed on soil samples from NPL sites are those listed in 40CFR 136 and the EPA Test Method for Evaluating Solid Waste (SW846) as:

- Priority Pollutant Scan
- Priority Pollutants + 40
- Extraction Procedure Toxicity test
- Partial scans of those three (e.g., Volatile Organic Analysis)

The priority pollutants and acutely hazardous substances that are listed in 40CFR 122.21, Appendix D, were grouped by the physical and chemical parameters that affect the ability of an extraction agent or process to mobilize them:

- Water solubility
- Octanol water partition coefficient
- Vapor pressure
- Density

These parameters were used to create separate lists of hydrophillic organic compounds, hydrophobic organic compounds, volatile organic compounds, heavy metals, other inorganics, and radioactive materials. Definitions of these contaminant classifications are:

- "Volatile"--having a vapor pressure at 25°C over 5 mm of mercury

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- "Hydrophillic"--having a solubility in water, at 25°C, over 10 g/L

- "Hydrophobic"--possessing an octanol/water partition coefficient (K_{ow}) greater than 100

- "Heavy metal"--having a density greater than 5 g/mL.

This choice of definitions makes some highly soluble contaminants both hydrophillic and hydrophobic, while very slightly soluble materials are neither. Professional judgment was used to assign a single classification to each contaminant. Since K_{ow} data are not available for all of these materials, some of the characterizations were based on statements in the reference literature like "slightly soluble in water, very soluble in benzene."

Physical property information used to determine contaminant classification were obtained from:

- The CRC Handbook of Chemistry and Physics

- The Handbook of Chemical Engineering

- The Condensed Chemical Dictionary

- Sax's Dangerous Properties of Industrial Materials

- The Handbook of Environmental Data for Organic Compounds

- The Merck Index of Chemicals

- The Chemical Profiles Appendix to the EPA Chemical Emergency Preparedness Program

SOIL CLASSIFICATION

Most extraction processes remove contaminants more quickly from coarse silica sand than from fine aluminosilicate clay. Attempts were made to characterize the soil present at each NPL sites, but because detailed information on soil type is not consistent in the files, gravel, sand, silt, clay, and waste fill were used as soil categories. The humus or organic matter in the soil was noted when that information was available.

SITE SURVEY REQUIREMENTS

The following information was obtained on each site to evaluate potential extraction technologies:

- Name of site
- Quantity of contaminated soil (including waste)
- Type of soil

- Types of contaminants present
- Concentrations of contaminants

The original search plan was to electronically search NPL site information databases maintained by EPA contractors. The most likely databases were identified by conferring with the personnel at CERCLA offices in Washington, D.C. The databases considered, the range of sites on the database, and the information they provide are:

- **MITRE Database:** Lists every NPL site and no other sites. The database contains information on site name and contaminants present in groundwater, surface water, and air; there is no information on soil type, soil quantity, or contaminants in soil.

- **Damage Incident Database:** Lists most NPL sites and many others. Information on site name, soil contaminants, contaminant concentrations, and quantity of contaminated soil is present, but there is no information on soil type.

- **NPL Records of Decision Database:** Lists 130 NPL sites. The database consists of information on site name, soil contaminants, contaminant concentrations, and quantity of contaminated soil; there is no information on soil type.

- **CDM CERCLA Waste Type Database:** Lists 59 NPL sites. Information encompasses site name, soil contaminants, and quantity of contaminated soil; no information is provided on soil type or contaminant concentrations.

Since no available electronic database contained the information needed for this study, a decision was made to directly examine EPA's files on as many NPL sites as possible. To save cost and time, a limited manual search of the files of NPL sites in New York, New Jersey, and Puerto Rico was performed.

These files were examined over 3 weeks at USEPA's Region II offices in New York City. The Region II CERCLA program monitors developments at 195 sites. The information on soil contamination was not adequate for soil washing in 56 of the files. Remedial/removal work was complete at 8 of the sites. Groundwater (as opposed to soil) contamination was the important consideration at 35 sites. No quantitative information on soil contamination was provided at groundwater sites. Other types of nonsoil contamination were important at 13 sites. At the remaining 82 sites, soil contamination data were adequate.

The data are not reported consistently from one EPA file to the next. Most of the concentrations reported as obtained are "eyeball averages" of many individual data points listed in raw data tables at the back of RAMP, POP, RI, FS, HRS, Phase I, or Phase II reports. The "eyeball average" was used because a simple arithmetic average would over-represent less contaminated soil that would be neither excavated nor processed. The type of soil was sometimes stated in great detail, as in an RI or FS. It was often only hinted at ("This property is swampy"). Because the goal of the study was to obtain a soil contamination pattern, a chance was taken of being wrong in a few individual cases to increase the number of sites listed. The quality of the data was considered good enough for a pattern study, but not good enough for work on individual sites.

APPARENT PATTERNS OF SOIL AND CONTAMINANT OCCURRENCE

The 82 sites that yielded adequate soil contamination data were included in the database for this study. If the Region II data are perfectly representative of the Nation, then soil contamination is important and documented at 295 of the 703 NPL sites.

There are 176 contaminant/soil-type matches recorded in Table 2. Only three contaminant/soil-type pairs occur more than twice the average rate--hydrophobic volatile compounds, hydrophobic nonvolatile compounds, and heavy metals--all of them in sand.

TABLE 2. TOTAL SOIL AND CONTAMINANT MATCHES AT REGION II NPL SITES
(number of sites/total Mm^3)

Contaminant	Sand	Silt	Clay	Waste
Phillic Volatile	12/0.31	3/0.01	4/0.01	7/8.99
Phillic Nonvolatile	4/0.51	1/0.61	1/0.56	2/0.91
Phobic Volatile	24/3.41	6/0.82	5/0.03	6/7.41
Phobic Nonvolatile	27/3.36	6/0.87	4/1.18	6/8.15
PCBs	4/0.47	1/0.01	2/1.15	1/0.05
Heavy Metal	20/6.42	8/1.18	3/0.43	10/1.72
Other Inorganic	2/0.05	1/0.01	---	2/4.59
Radioactive	1/0.21	1/0.04	1/0.01	1/0.06

The removal of contaminants is more likely to succeed in sand than in clay or waste. These findings suggest that a process that works with sand alone is very useful. Sand sites may affect ground water contamination more than clay sites. The number of sites and the volume of soil to be cleaned are sufficient to guarantee extensive opportunities to use any soil extraction technology that can successfully remove one or more of these contaminant types from sand.

Of course, the presence of one class of contaminants may impede removal of another. Figures 1, 2, and 3 plot the contaminant level (ppm) vs. the amount of contaminated soil for volatile hydrophobics, nonvolatile hydrophobics, and heavy metals in sand. A typical site is about 40,000 m^3 of soil with levels between 100 and 1000 ppm. No judgment can be made about the significance of multiclass contamination until a specific process is under consideration.

REGION II SITE SURVEY
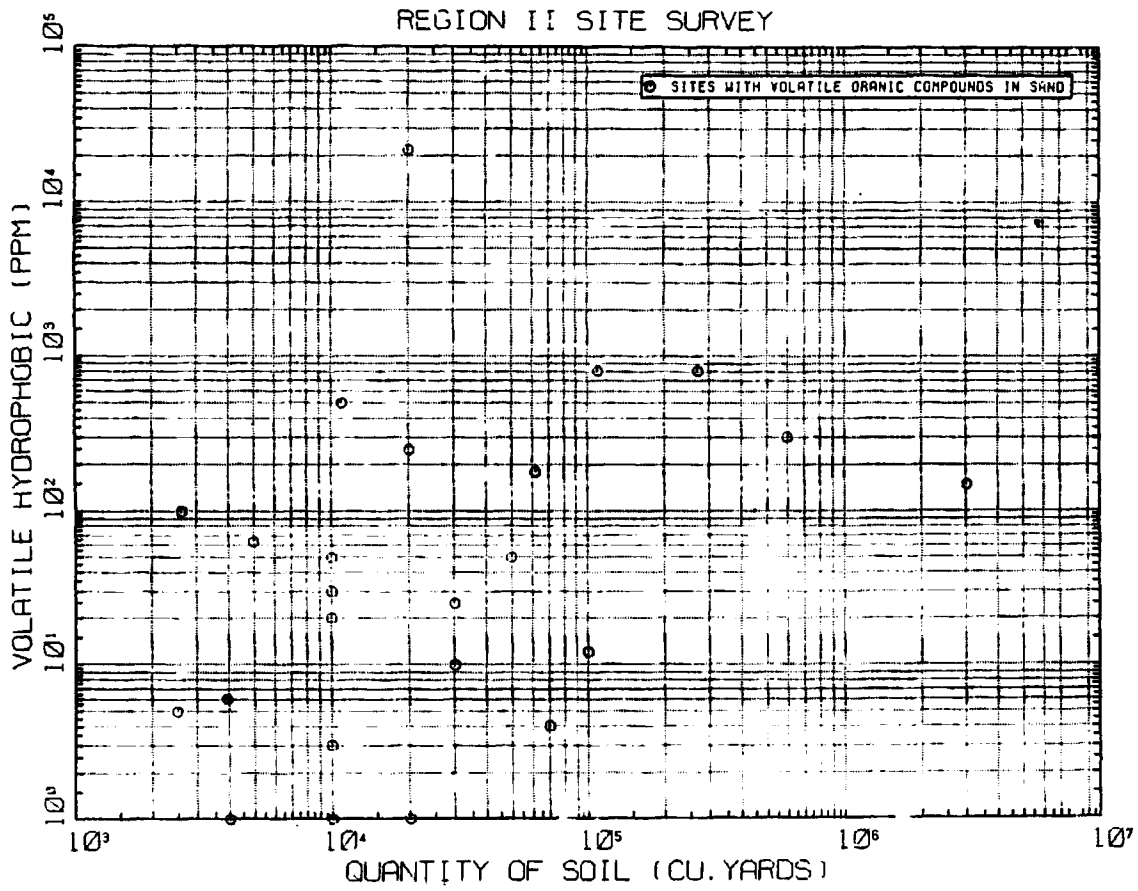
Figure 1. Volatile hydrophobic soil contamination concentration vs. quantity of soil.

REGION II SITE SURVEY
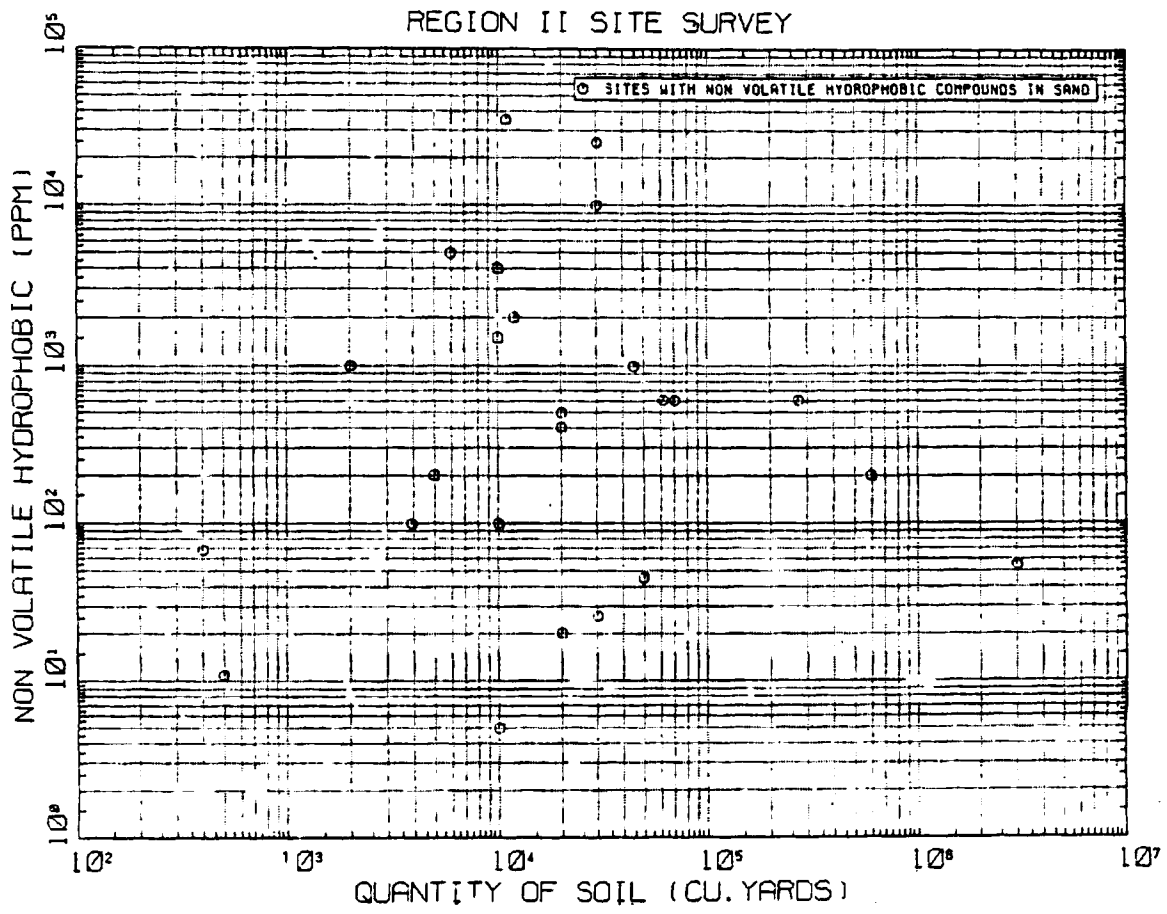
Figure 2. Nonvolatile hydrophobic soil contamination concentration vs. quantity of soil.

REGION II SITE SURVEY
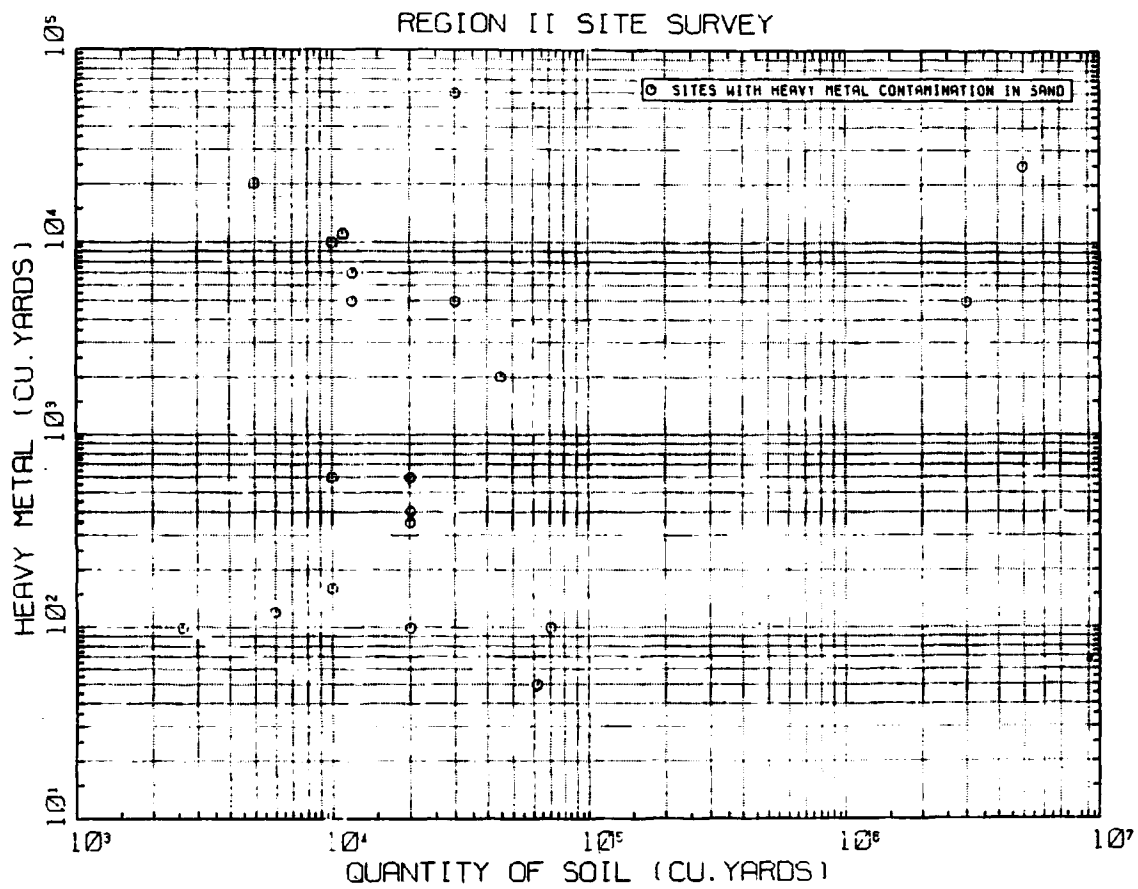
Figure 3. Heavy metal hydrophobic soil contamination concentration vs. quantity
of soil.

SECTION 3

EXTRACTION TREATMENTS TO CLEAN SOIL

PROCESS CLASSIFICATIONS: AN OVERVIEW

There are three general extraction treatments for cleaning contaminated soils:

• Water Washing with Agents

- Surfactants that improve the solubility of the contaminants

- Chelating additives used to chemically react with metals

- Acid or alkaline solution to mobilize, neutralize, or destroy the contaminant

- pH control to improve solubility

• Solvent Extraction of Organic Contaminants

- Organic solvent mobilizes the contaminant into the bulk part of the solvent

- Sonic vibration or vigorous mixing improves the mobility of the contaminant into solution.

• Volatile Organic Contaminant (VOC) Stripping

- Agents such as steam or air

- Heat, vacuum, or both increase the extraction rate.

These extraction treatment classifications encompass the information found in the literature concerning cleaning of contaminated soil above ground. The relationship between extraction treatment and contaminant classifications is given in Table 3.

TABLE 3   EXTRACTION TREATMENT VS. CONTAMINANT CLASSIFICATION*

Extraction Treatment	Contaminant Classification					
	Hydro- phillic Organics	Hydro- phobic Organics	Volatile Organics	Heavy Metals	Other Inorganics	Radio- active
Water Washing Agent						
pH Control	x					
Surfactants	x	x				
Chelation				x		X
Acid or Base		x		x	x	x
Solvent Washing		x				
VOC Stripping			x			

* Based on experimental treatment processes that have been proved effective on specific contaminants; however, none are offered commercially to clean soil.

The information discussed in this section was obtained from the open litera- ture. Water washing of soils with chelating agents and surfactants has received some recent interest in the area of bench-scale and pilot plant scale testing. The use of acids and bases to remove metals and organics from contaminated soils has met with limited success. Soil washing with organic solvents has not been tried, but solvent extraction equipment is available for other applications. This equipment is discussed as it applies to cleaning soils. Volatile organic stripping of soil has been explored to a limited extent. The equipment required for this type of extraction of the volatiles from soil is discussed.

WATER WASHING WITH EXTRACTION AGENTS

Water-Based Washing Solutions

Washing solutions are basic aqueous solutions (caustic, lime, slate lime, or industrial alkali-based washing compounds), acidic aqueous solutions (sulfuric, hydrochloric, nitric, phosphoric, or carbonic acids), or solutions with surfactant or chelating agents. Hydrogen peroxide, sodium hypochlorite, and other oxidizing agents are also used to chemically change the contaminants. A strong basic or surfactant solution can be used for organic extraction, and strong acidic or chelating agent solutions can be used for metal extraction. Strong base or acid might be used in cases of high contaminant concentration, where the cost of chemicals is affordable and the wastewater can be treated for safe disposal. Surfactant and chelating agent soil cleaning are being developed to reduce chemical and equipment costs, make the soil reusable, and simplify wastewater treatment. The surfactant and chelating solutions have a moderate (almost neutral) pH, making equipment operation safer. The successful development of a means to clean soils with surfactants and chelating agents is important because most soils at NPL sites are contaminated with organics and heavy metals.

Equipment Unit Operation

Rulkens, et al., proposed a general block diagram form of the equipment train used to extract contaminants from excavated soil (Figure 4) [134]. For each unit operation, commercially available types of equipment and processes are discussed in the reference.
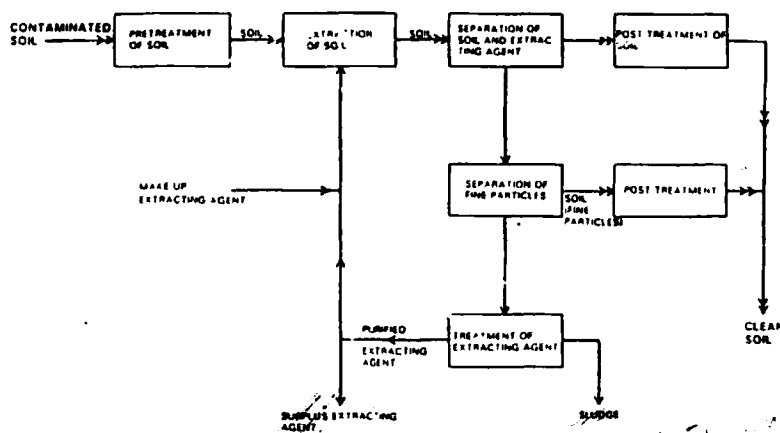
Figure 4. General block diagram for soil cleaning.

To date, no aqueous extraction system for cleaning excavated contaminated soil has been successfully (or even unsuccessfully) demonstrated on a large scale. However, there has been some success in the laboratory and some limited pilot scale experience. In general, work involved in demonstrating equipment unit operation pertains to pretreatment and extraction of contaminated soil and post-treatment of the extractant. The effective separation of the extractant from the soil, recycle of the regenerated extracting agent, and concentration/ destruction of the contaminant have not been demonstrated on a large scale pilot facility.

Soil Pretreatment and Extraction Equipment Experience--

Netherland's Bromide Removal From Sand Pilot Study [32]--Sandy soil containing less than 10-percent clay and humus was cleaned by a 2:1 caustic solution (pH >11). The soil was pretreated by grinding in a pen mill to reduce the size of soil clods. A 1 ton/h inclined (30-deg) screw conveyor was used to extract the contaminant and separate the extractant from the soil. The soil

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and fresh extractant were fed into a hopper at the lower end of the screw.
The spent extractant was removed as overflow from the hopper, and the clean
soil was discharged from the screw top. The test information was used to en-
gineer a future on-site treatment plant.

Lee Farms Lead Extraction From Soils [93]--The lead-contaminated soil at
an NPL site was screened to 3/4 mesh and crushed to 50 mm x 0. The crushed
soil was washed by a 30-percent EDTA solution, using an inclined-screw washing
unit. One part of soil was mixed with three parts of extractant in a hopper at
the lower end of the screw. The equipment was operated solely as a batch unit
because the soil contained too many fines, overwhelming the ability of the equip-
ment to continuously separate the clean soil from the extractant. The test in-
formation is being used to specify equipment that can handle clays for future
pilot plant work at this site or other NPL sites.

EPA's Mobile System For Extracting Spilled Hazardous Materials From Ex-
cavated Soil [45,46]-- Pilot studies were performed to determine the equipment
train. Three unit operations were developed and proved by testing:

- **Water Knife Concept**--A thin, flat, high-speed jet was optimized to break up
  clumps of soil and scrub contaminants from larger soil particles like stone
  and gravel. Testing showed that this concept is very effective.

- **Rotary Drum Screener**--A rotary drum was employed as a pretreatment to mix
  the soil with the extractant.

- **Extraction and Separation Concept**--A four-stage counterflow extraction train
  was designed and built. Each stage consists of a tank, stirrer, hydroclone,
  and circulating pump. The pump moves the soil from one stage to the adja-
  cent stage. The hydroclone discharges the soil slurry in the next stage
  and returns the extractant. The extractant flows by gravity as a tank over-
  flows in a stream from one tank to another counter to the direction of the
  soil. Fresh extractant is added to the fourth stage and spent extractant
  removed from the first stage.

Hot Water Process for Extraction of Oil From Tar Sand [166]--The sand is mixed with hot water and violently agitated to mobilize the oil. The sand/oil mixture is continuously separated in a settling tank. The oil froth overflows the tank and is separated by a centrifuge. Water is added to the centrifuge to form a barrier between the oil and sand.

Gasoline Removal From Sand [177]--A fixed-bed pilot test program was sponsored by the American Petroleum Institute using a sand bed. Surfactants were used to enhance the recovery of gasoline. The sand bed was about 3 m^2 by 1.2 m deep. Multiple applications by percolation resulted in good recovery of the gasoline.

This limited experience with pilot-size equipment indicates that sandy soil probably can be processed, using a washer-dewatering inclined screw [202]. The processing of clays and silts has not been demonstrated and would involve developing equipment to handle these soil fines.

Equipment for Post-Treatment of Extractants and Soil [58]

Treatment of the contaminanted extractant is required so that purified water and recovered additives can be recycled. Processing of a contaminated extractant is similar to processing polluted water, which is a mature science. Equipment is readily available for the following processing unit operations:

Biological Treatment--Most organic contaminants can be destroyed biologically. Work at Rutgers University is extending this established treatment concept to the field of hazardous waste [142,143]. The key unit operation is a biological treatment bed for destroying organic chemicals in an aqueous extractant.

Coagulation and Sedimentation [141]--Additions of coagulant and flocculant aids to the contaminated water can separate the contaminant from the water. This technique is also useful for removing fine soil particles from the treatment fluid.

Ion Exchange--This technique is usually a polishing treatment for low levels of ionic-type contaminants. In the case of radioactive contaminants, the technique applies as a primary cleaning method.

Activated Carbon--Most organic contaminants are removed from water using the carbon filter. This technique is the most useful in concentrating the contaminant and cleaning low levels of toxic organics.

Supercritical Oxidation [201]--This extreme wastewater treatment process is very effective in destroying all organics. Oxygen is added to pressurized contaminated water. The water is heated above the critical point to destroy the contaminant. An additional benefit is that some inorganics separate out from the supercritical water. End products are innocuous: N_2; CO_2; H_2O; salts such as $CaSO_4$, $MgSO_4$, and Fe_2SO_4; and clean water.

Photochemical Destruction [24,202]--Ultraviolet light enhances chemical reaction rates. This technique allows for destruction of organics at moderate temperature. Oxidizing agents are added to enhance the destruction of organics.

Oxidizing Agent [197]--Oxididizers such as bleach, hydrogen peroxide, and ozone are used to destroy organics.

Electrolysis [43]--Electrolysis provides the means to regenerate the chelate and recover the metal.

Volatile Stripping of Organics From Water [166]--Volatile organics can easily be stripped from water in a scrubbing tower. The contaminant can be either vented to atmosphere or destroyed by incineration.

Filtering--Fine particles in the extractant can be removed by a filter. The use of sand, diatomaceous earth, or other type of porous disposable layers might be required instead of conventional reusable filter material because soil fines may permanently plug the filter material.

These post-extractant treatments have not been demonstrated because of the lack of pilot plant operating experience on a complete above-ground soil cleaning facility.

The post-soil treatment is usually necessary to eliminate any threat that the contaminant will leach after reburial. The cleaning method may make the remaining less-concentrated contaminant in the soil more mobile than the original more concentrated contaminant in the soil before cleaning. These polishing procedures are possible:

- Rinse soil with water
- Reduce the remaining environmental hazard by chemical fixation or reaction
- Deposit soil on the surface of the ground and farm the soil.

Procedure For Washing Contaminants From Soil

Hydrophillic Organic Contaminants--

    Definition--A hydrophillic organic is defined as being soluble in water.

However, each compound has its own solubility limit. The containment level at

NPL sites is sufficiently low to go into solution. There is a high frequency

of occurrence of nonvolatile organic such as phenols, and typical volatile com-

pounds are methylene chloride and aldehydes. The volatile occurrences outnumber

the nonvolatile cases 3:1.

    Process Parameters--

- pH--For some organics pH is a useful variable to improve the mobility of the
  contaminant into solution. For example, phenols are easily mobilized with
  an alkaline solution. Reverse changes in pH can be used ro separate the or-
  ganic from water in a post-extractant treatment step.

- Humic Content in Soil--Humus in soil contains bonded water, colloids, and
  chelates that retain the contaminant. A caustic solution is used to free
  these contaminants by breaking down the humic material.

- Agitation--A turbulent mixing process is required to intimately disperse the
  soil in the washing solution and to provide abrasion to break down inhibiting
  film conditions in the soil.

- Time, Soil Loading, and Staging--Extraction time may be a more important
  variable than water to soil ratio or number of extraction stages. The
  economics will dictate the design specifications of these variables.

- Wetting Agent--A wetting agent may be required to improve the penetration
  of the water into the soil particles to mobilize the contaminant.

    Previous Experience--Hydrophillic contaminants are effectively removed by

in-situ washing. Therefore, the opportunities for above-ground cleaning are

limited. The only mechanism for binding hydrophillic content is the presence

of humus in the soil. A percentage of humic material (colloids) above 1 per-

cent and high contaminant levels may require above-ground treatment.

Hydrophobic Nonvolatile Organic Contaminants--

<u>Definition</u>--A hydrophobic organic is defined as being insoluble in water.

However, some hydrophobic organics with an octanol/water partition coefficient

between 10 and 1000 are referred to as "slighly hydrophillic." These organics

tend to be found in the ground water because of natural washing by ground water

movements. The slighly hydrophillic organics are more easily washed than the

less insoluble organics. Typical slighly hydrophillic compounds are aromatics

and halogenated hydrocarbons. Commonly found insoluble hydrophobics at NPL

sites are halogenous aromatics, pesticides, heavy oils, and greases.

<u>Process Parameters</u>--

- <u>Surfactants</u>--Surface active agents are added to the water to reduce the
  surface tension between two liquids or a liquid and a solid. The addi-
  tive should be for effective liquid/liquid interface, but not for liquid/
  solid interface because the fine soil particles become dispersed in the
  extraction solution. Surfactants provide the link between water (a polar
  compound) and the hydrophobic contaminant (nonpolar compound). If the
  contaminant were immobilized by porous soil particles, the surfactant
  might not mobilize the contaminant into the water; the mobilization has
  to be done with an organic solvent. Combinations of water, surfactants,
  and organic solvent additives are required. Aqueous surfactant washing is
  not applicable to soils with a high humic content.

- <u>Caustic Agent</u>--Soils high in humic content require a high pH solution (>12)
  to mobilize the contaminant from the humus. The caustic breaks down the
  organic structure and mobilizes the contaminant if the contaminant does not
  react with the caustic to form an insoluble compound.

- <u>Extraction Stages</u>--More than one extraction step is required. The contami-
  nant level should be reduced by one order of magnitude per step. The re-
  sidence time in each step should be long enough to achieve this reduction.
  The hydrophobic contaminant level at NPL sites varies between 100 and
  10,000 ppm and thus may require two to four stages of extraction.

- <u>Agitation</u>--Mixing is required to disperse the soil, but excess mixing will
  produce large amounts of sludge. The mixing should only aid in mobilizing
  the organic, not disintegrate the soil.

- Temperature--A temperature near the boiling point of water (can be a slightly pressurized system) should aid in mobilizing the contaminant. The contaminant is removed as a froth from each stage.

- Reactor Configuration--For contaminants that are slighly hydrophillic and permeable, a fixed-bed arrangement is satisfactory. For insoluble hydrophobics, a constantly stirred reactor is required.

- Solid-to-Extraction Solution Ratio--A ratio of one part solids to one part extraction fluid is preferred to minimize the treatment of the extractant. However, two to three parts of extraction fluid is a more practical range with respect to equipment operation.

Previous Experience--The most recent and thorough investigation of aqueous surfactants used for soil cleaning is discussed in a report by Science Application International Corporation (SAIC) [50] sponsored by EPA. A sandy soil with low humic content (<1/2 percent) was spiked with two hydrophobic compounds-- crude oil and transformer oil containing PCBs. Crude oil (1000 ppm level) was reduced by 93 percent using 2 percent each of Adsee® 799 (Witco Chemical) and Hyonie® NP-90 (Diamond Shamrock) surfactants. The extent of removal of PCBs was 92 percent for 0.75 percent of each surfactant.

The work that served as a basis for the SAIC work was performed by Texas Research Institute [177]. Gasoline was recovered from sand in a pilot study by percolating an aqueous surfactant solution through a bed of gasoline-contaminated sand using a combination of commercially nonionic (Hyonic® PE-90) and anionic (Richonate® YLA) surfactants. Multiple washing recovered 76 percent of the gasoline.

Heavy Metals Extraction Using Chelating Agents--

Definition--All metal cations have one or more coordination numbers representing the amount of "reactive" sites available to ligands (group intimately

surrounding the cations). An interaction occurs at coordination sites between positively charged metal cations and electron-donating ligands to form complexes [a]. Chelants are ligands with function groups that form multiple chemical bonds in a ring structure [51]. Chelants react with metals in ionic form only, not in a free metallic state.

Process Parameters--

● Chelation (an equilibrium reaction)--Chelation may be defined as an equilibrium between a metal ion and a complexing agent, characterized by the formation of more than one bond between the metal and a molecule of the complexing agent and resulting in a ring structure incorporating the metal ion.

● Effect of Other Metal Cations--A stability constant measures the affinity of a metal for a particular chelant. The greater the affinity, the greater its ability to displace other chelated metals. This preferential chelation occurs at a thousandfold stability difference between metals [189]. Naturally occurring soil-bearing metal cations compete with the metal ions; however, proper pH control may minimize this effect.

● Effect of Other Anions--Anions have little effect on chelation; however, sulfide anions form very stable metal sulfide complexes, which may be useful in regenerating spent chelation solutions.

● Soil Classification--Process problems resulting from the silt/clay soil fraction have been encountered in previous efforts to extract lead from soil [190-193, 61]. Solid/liquid separation difficulties and failure to decontaminate the silt/clay fraction can be eliminated by classifying soil into its substituent fractions before or during chelation. Remediation methodology and equipment can be adapted to each classified fraction.

● Temperature--Temperature has a negligible effect on chelation. Chelant-metal complex stability decreases one order of magnitude per 55°C increase [189].

● Ionic Strength Effect--An ionic equilibrium exists between the chelant-metal complex. A large concentration of ions not participating in chelation lowers the complex stability, however, the effect is negligible [189].

● Chelant Concentration--The amount of chelant needed to react with a unit weight of a specific metal is provided in manufacturers' literature, and they recommend this quantity be verified by laboratory tests [189]. For

continuous processing of soils, additional considerations in determining chelant quantity are chelant solution viscosity and the amount of chelant needed to drive the reaction to completion.

● Chelation Duration--If the objective is to chelate the maximum amount of metal, then empirical determination is necessary to obtain the reaction duration.

● Soil Loading--The chelating solution-to-soil ratio must be high enough to allow proper mixing; however, as the ratio increases, reactor size, number, or both increase. If the chelant-soil mixture reaches chemical equilibrium, soil loading must be balanced with spent chelant removal and fresh chelant introduction rates.

● pH--pH is one of the most important parameters of the system. Both metal cation and chelating agents are influenced by hydrogen ions; hence any change in pH affects the equilibrium of the system [189]. Since stability constants are pH dependent, an adjustment of solution pH may favor the formation of a preferred metal complex. For example, pH 7 to 9 favors lead reaction over the generally more stable Fe (III), so contaminated soil may be treated without significantly extracting the ubiquitous iron.

Previous Experience--Metal chelation research has examined the metals-soil binding and metal availability for plant removal of metal from the soil . Soil treatment research has focused on in-situ metals chelation with low-concentration, mild extractants. Limited extraction work on excavated soil has yielded encouraging metal-reduction results, but has encountered soils-handling problems. DTPA sludge extractions by Silviera and Sommers yielded maximum removals of 50, 29, 40, and 30 percent for total Pb, Zn, Cd, and Ca [77]. Brown, et al., reported the percentage of extractable metals for plant removal in sludge-treated Padina soil was as high as 105, 84, 56, 178, and 46 percent for Pb, Zn, N, Cd, and Ca [9].

In EDTA chelation experiments for in-situ treatment, Connick, et al., pre-adsorbed metal salts onto typic hapludult soil contained in columns and rinsed with 0.144M EDTA, achieving 63-, 93-, 94-, 100-, and 82-percent removal of Pb,

Zn, Ni, Cd, and Cu [49,57]. During metal-soil leaching studies, extraction of preadsorbed clays by Farrah and Pickering showed EDTA effectiveness on the strongly binding clay fraction [80]. Some researchers assert that metal-soil binding changes with time until an equilibrium is established [9,57]; hence preadsorbed soils used in the previous extraction studies may not be representative of "mature" NPL soils. Ellis and Fogg used an EDTA/hydroxylamine/citric acid sequential extraction for in-situ remediation of Western Processing, Inc., NPL site soil, reducing Pb, Ni, Cd, Cu, and Cr by 96, 22, 100, 75, and 52 percent [51]. Their multiagent extraction was more effective than a single-step EDTA chelation because a greater range of metal binding mechanisms was vulnerable to release.

Other chelants reduced lead content in soil. At Church of God in Leeds, Alabama, by 95 percent with ammonium pyrolidinecarbodithioate (APOC) [61]; and PEI Associates reported that "NTA did not work as effectively as EDTA" in chelating lead from the soil at the Lee Farm in Woodville, Wisconsin, during laboratory studies [194].

Recent pilot scale chelation studies on excavated soils have produced promising results; however, several obstacles must be overcome. U.S. Environmental Protection Agency, Releases Control Branch (USEPA) and International Technology Corporation (IT), utilizing 13-16 percent EDTA chelant, removed 94 to 97 percent of total lead from Church of God soil using the 4 to 5 ton/h capacity screw extractor. At the Lee Farm, USEPA Region 5 and PEI Associates reduced gross lead contamination below the EP Tox limit of 5 ppm leachable lead in laboratory scale EDTA chelations. However, during production-scale treatment, the broken battery casing fraction alone was decontaminated below EP Tox requirements [190,191,194].

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Soil-handling problems at both sites included:

- Blending plate/frame and filter because of silt and clay

- Plugged pumps, worn augers, and difficulty in handling sands

- Large quantities of chelation solution carry-over into rinse tanks

- Solid/liquid separation of silt and clay between process steps

To eliminate some of the problems encountered at the Lee Farm, Enviresponse, Inc. (EI), under USEPA Emergency Response Team (ERT) auspices, classified Lee Farm soil into fractions (>1/4 in., 100 microns to 1/4 in., and <100 microns) before laboratory EDTA chelation. They achieved 700 ppm residual total lead in the 100 micron to 1/4 in. fraction, a 95-percent reduction, while maintaining EP Tox values within limits [6]. By adjusting the EDTA solution to pH 7, thereby maintaining a high stability constant for lead over iron, these researchers chelated little Fe (III) in the high-iron-bearing soil.

Heavy Metals Extraction Using Acids and Other Extracting Agents--

Definition--Acids that demobilize soil-bound metals in an ionic solution [80].

Process Parameters--

- Extractant Type--Factors to consider in choosing an acid are effectiveness, safety, disposal, and cost.

- Extractant Concentration--Acid extractant concentrations have varied greatly (e.g., 0.001M HNO_3 to concentrated HNO_3) [8,80]. If a mobilization ion-exchangeable metal is required, then proton-excess is required. If the release of metals occluded in coprecipitates as oxides and sulfates is desired, higher acid concentrations are necessary. The literature reported that extractant concentrations vary greatly; therefore, experimental data are necessary to determine the appropriate concentration to obtain a desired reaction product.

- Soil Loading--As with soil chelation, the extractant-to-soil ratio should allow for intimate mixing. The soil loading should be low enough to allow maximum metal extraction at a particular extractant concentration.

Previous Experience--Singh and Karwad [8] state the following order of ex-
traction performance: on sludge treated soil conc, HNO_3 > Aqua Regina >
0.2M HCl > 1M NH_4OAc (pH 4.8). However, the different concentrations make
acid comparisons difficult. A treatment study at the Celtor Chemical Works site
in Hoopa, California, utilizing very high-strength acids found "none of the ex-
tractants were capable of producing a soil below clean-up level for all met-
als" [185]. This study reported lead removals were up to 44 times greater for
hot HCl vs. ambient HCl, and the removal pattern for HCl/H_2O_2 was similar to
the pattern for HCl. On the other hand, an ammonium carbonate-fluosilicic acid
extraction of the Lee Farm classified soil (100 micron to 0.64 cm fraction) was
performed by Cole at the U.S. Bureau of Mines in Rolla, Missouri. This process
reduced total soil lead to 500 to 800 ppm--a 94-percent reduction [193,202,203].

A German process extracts heavy metal from dredged harbor sediments. Known
as the "leaching process of Müller", the process extracts heavy metals with HCl,
separates solids from extractant, and removes heavy metals from the acid solu-
tion by hydroxide and carbonate precipitation [28].

Extraction of Radioactive Materials--

Definition--Because radioactive contaminants are chemically similar to heavy
metals, they can be treated in a similar manner.

Process Parameters--Parameters for effective radioactive contaminant treat-
ment are the same as for heavy metal treatments.

Previous Experience--Numerous extractants, inorganic and organic, have
been examined to decontaminate radioactive soil, with some favorable results.

Pishita, et al., used 21 inorganic compounds, 5 organic acids, and DTPA to remove PU 239 from preadsorbed soil [68]. $Na_4P_2O_7$, the most potent inorganic extractant, removed 28.6 percent and sodium citrate extracted 89.9 percent of the PU 239. However, a DTPA solution of 0.004M was more effective than a 0.08M citric acid solution. Spalding removed >95 percent of Sr 85 from Oak Ridge Solid Waste Storage Area soil with a sequential extraction consisting of 1M KCl, 0.1 HCl/0.5M KCl and 8M HNO_3 [66]. Soil composition does play a major role in extractability. PU 239 was least mobilized in low-organic soil because of strong sorption on the inorganic fraction [69]. According to Nashita, et al., "soil organic matter, free iron oxides, silica, alumina, and amorphous aluminasilicates influenced the extractability of PU 238 and Cu 242" [70]. pH had a substantial effect on their extractions. The extractability of Cu 242 greatly increased below 2 to 3 pH and moderately increased around 12 pH; below 2 pH, Pu 238 extractability increased only slightly, yet a significant increase occurred at about 12 pH. These researchers concluded that at a pH below 4.5, Pu 238 was more strongly adsorbed on the soil mineral fraction.

SOLVENT EXTRACTION OF HYDROPHOBIC ORGANIC CONTAMINANTS

General Process Considerations

The choice of suitable solvent depends primarily on solvent extractive capacity and equilibrium characteristics. In addition to these, the solvent should be stable and must have favorable density, viscosity, and interfacial tension properties. There should be a sufficient difference between the boiling points of the solute and the solvent to aid in post-treatment separation.

In general, the ideal solvent for the task should not be volatile at low temperatures; should be pure, noncorrosive, nonviscous, nonfoaming, nontoxic, noninflammable; should have infinite solubility for the solute(s); and should be inexpensive [159: lists possible solvents for different contaminants].

Process Unit Description (might apply to soil cleaning)

Solvent extraction of the organic contaminant takes place in one or a series of pieces of equipment called extractors. The equipment, as well as the general arrangement of the plant, is highly dependent on the nature of the contaminant and its relative solubility in the chosen solvent. Leaching and immersion extraction are the two extremes:

Leaching--

In its most typical form, leaching is a batch extraction in which the screened soil is deposited in a false-screened bottom tank(s) inside retaining walls and solvent is sprayed over it. The solvent leaches the contaminant from the soil. The contaminant-rich solvent is collected at the bottom after it has percolated through the soil. In the absence of agitation, the liquid-solid extraction is slow and not very efficient. Liquid channeling through the soil can further lower the extraction efficiency, leaving a portion of the soil unextracted. The presence of fines can stop the percolation process. On the other hand, coarse agglomerates with a well-imbedded contaminant often can be cleaned at the surface only. At the end of the extraction process, the soil retaining the solvent is dropped through the false bottom and another batch is started.

For a single batch extractor, contaminant-free solvent is sprayed until the bottom solvent shows no traces of contaminant and the extraction can be considered total. The process is slow and requires large amounts of solvent; the rate of extraction decreases with contaminant concentration.

To overcome these disadvantages, a battery of extractors can be operated in countercurrent extraction. The more fully extracted soil is leached with fresh solvent; the fresh soil is the last in the extraction line.

Immersion--

For low-solubility contaminants, fine soils like clay and silt, or a very low residual contaminant content, the leaching process is unacceptable. For these cases the solid is intimately dispersed into the liquid in so-called <u>immersion</u> extraction.

In its simplest form, an immersion extractor is an agitated tank filled with the solvent, in which the soil is suspended and thoroughly mixed. When the extraction equilibrium has been reached, the agitation is stopped and the solid is allowed to settle. The solvent is drained and fresh solvent can be used for a second-step extraction. The countercurrent extraction concept described for leaching extraction also applies for immersion extraction.

Soil-Solvent--

Soil-solvent separation can be a simple unit operation or a cumbersome series of unit operations. For coarse, easy-draining soils such as gravel and sand, the solvent is just drained from the soil. For hard-to-settle fines, such as clay or silt, the operation will require mechanical solid-liquid centrifuges.

Residual Solvent Elimination--

Granular solids retain liquids because of surface adherence forces and interstitial surface tension forces. The higher the viscosity and surface tension of the liquid and the smaller the granules of the solid, the more solvent is retained in the solid bed. Chosen solvents are expected to have low viscosity and surface tension, which will reduce liquid retention. Fine soils, high surface adsorption materials, or colloidal suspensions tend to retain large amounts of solvent.

The best soil is a coarse sand which will retain, at free gravity drainage, approximately 2 to 3 wt% solvent.

Solvent Displacement--

Most (if not all) of the possible organic solvents are undesirable (soil) contaminants and, regardless of the cost of the lost residual solvent, must be eliminated from the soil before reburial. (Some examples of elimination processes are solvent displacement, gas or vapor stripping, and temperature stripping.)

Solvent displacement is another solid-liquid extraction where the new solvent is nontoxic and is left in the soil. The initial extraction solvent must be totally miscible with the displacement solvent. The least expensive and most nontoxic displacement solvent is water. Unfortunately, most good organic solvents (e.g., hydrocarbons, halogenated hydrocarbons) are not soluble in water, and this method cannot be applied. Alcohols, ketones, and esters are classes of solvents with high miscibility with water; consequently, displacement of

the residual solvent with water is possible. Process considerations and equipment used for solvent extraction also apply for this displacement process. Gas or vapor stripping and temperature stripping are processes similar to Volatile Organic Contaminants stripping, described in detail later.

Solvent Recovery--

Environmental and economic considerations require solvent recovery and re-use of the recovered solvent. As initially discussed, to obtain a high level of solvent recovery, a recommended solvent must have a relatively low boiling point quite distant from the contaminant boiling point. The most used and recommended solvent recovery method is distillation. The recommended solvent need not be totally contaminant free. Small amounts of contaminant may be recycled in the soil extraction.

Another possible, but not likely, solution for solvent recovery is a chemical reaction of the contaminant with the formation of a precipitate, an immiscible phase, or a nontoxic component. In these cases a precipitate can be separated by filtration and a nonmiscible phase by liquid-liquid separation; the nontoxic compound can be left to accumulate in the recycled solvent until its concentration interferes with the extraction process.

Previous Related Experience

Previous experience in commercial solid-liquid extraction applied to large amounts of solids includes ore, tar sand, and sugar beet extraction. In all these processes, the extractor contributes substantially to the capital and operating cost of the whole plant. Consequently, a substantial engineering

effort has been put into developing continuous extractors. Theoretically,
continuous extraction can be operated cocurrent, crosscurrent, or countercur-
rent. Consideration of the depth of extraction and solvent consumption have
imposed the countercurrent extraction as the only commercially acceptable
option.

Starting from the battery of extractors concept, Dravo Corporation devel-
oped the ROTOCEL EXTRACTOR®. In this extractor (Figure 5), the material to be
extracted is fed continuously as a slurry with the extraction solvent or as a
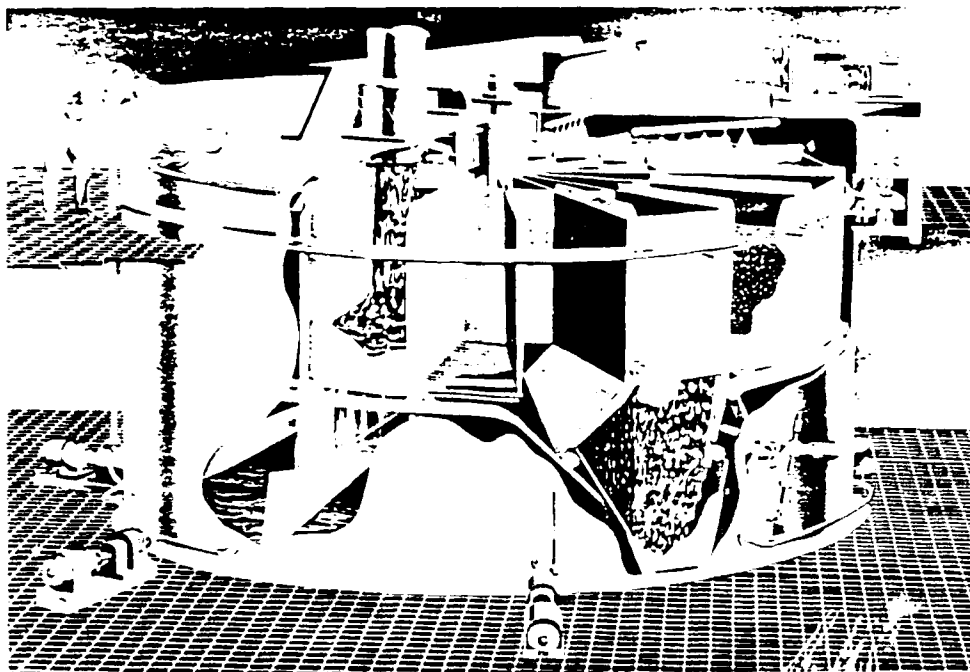dry feed to sector-shaped cells arranged around a horizontal rotor. The cells

Figure 5. Rotocel percolation extractor. Courtesy of Dravo Corporation [181].

have a perforated base to permit the solvent to drain into stage basins, from which it is pumped to the next cell on the countercurrent principle. In the last cell, where fresh solvent is supplied, an extended drainage period is provided (by allowing a proportionately larger arc of the rotary motion for this cell); thereafter, the extracted solids are dumped. In addition to being filtered by the bed of material being extracted, the fines are filtered over a tent screen before complete solvent removal. Rotary extractors similar in principle to the Rotocel are offered by other equipment manufacturers. Filtration of the fines over a bed of coarse material has been claimed to achieve solvents with less than 5 ppm suspended solids [181].

Another continuous extractor is the ENDLESS-BELT EXTRACTOR®; its principle of operation is closely related to the Rotocel. Extraction time and percolation rate determine belt speed and the drainage area required. Since bed height is virtually fixed by the mechanical design of the extractor, these parameters control the plant capacity. A low percolation rate could make the required drainage area prohibitively large. Solvent, which can be fed by spraying or simply from overflow weirs, may be used in a simple counter-current manner or, where the percolation rate is high, may be recycled internally to improve the approach to equilibrium [181].

The LURGI FRAME-BELT EXTRACTOR® (Figure 6) has a two-tier system in which the solid material travels the length of the extractor while being extracted in an upper series of compartments (frame buckets) with the perforated endless belt serving as a false bottom. The bed is then partially drained of solvent
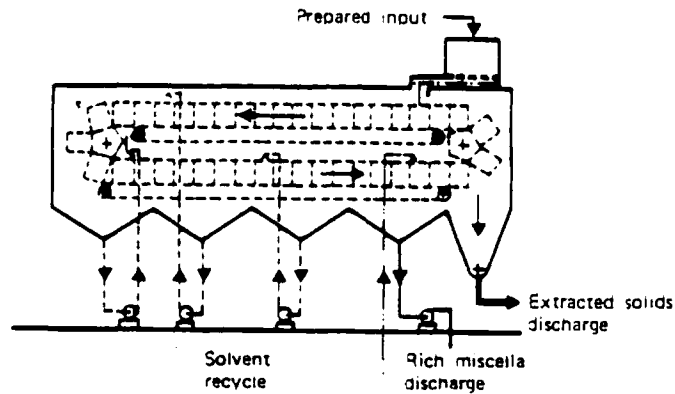
Figure 6. Lurgi frame belt extractor. Courtesy of Lurgi Umwelt und Chemotechnik G.m.b.H [181].

and discharged into a lower series of compartments. There extraction continues with an increasingly leaner solvent until reaching a final drainage zone before discharge of the exhausted solids [181].

The DE SMET BELT EXTRACTOR® (Figure 7) uses a single, endless belt to hold the material being extracted. The risk of solvent migration is minimized by

Figure 7. DeSmet continuous-belt extractor. Courtesy of Extraction deSmet, S.A. [181].

rakes that penetrate the upper 150 mm of the bed (overall bed height 1.3 to 1.8 m) to form ridges of solid material at intervals. The 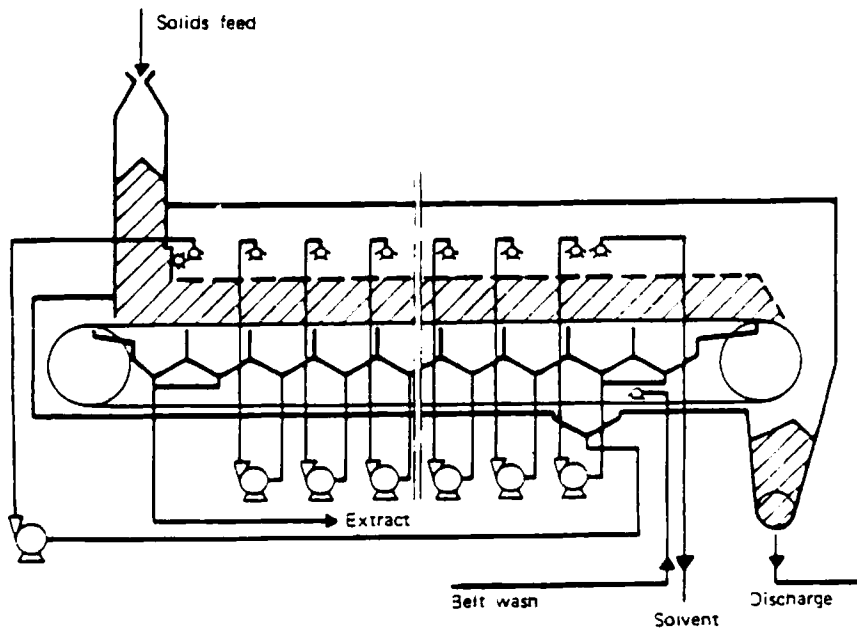rakes also break up the upper layer of the bed to maintain steady percolation conditions. The belt moves discontinuously, providing a clearly defined extraction period followed by a drainage period, continuing until the following spray is reached [181].

The ability of the immersion extractors to handle fines and to extract materials with low diffusion rates, makes this the process used for the extraction of sugar beets, oil seeds, or trace pigments and pharmaceuticals from plant materials. Continuous immersion extractors were originally constructed in tower forms, and such designs have maintained an important place in the sugar industry.

The BMA DIFFUSION TOWER has a central shaft fitted with a series of inclined plates that direct movement of the solid material. The tower shell is also fitted with a series of staggered guide plates that serve the same purpose. Another tower extractor, in this case designed and built by Wolf, also employs the principle of wings attached to the central shaft to transport the solid material to be extracted up the tower. In both cases sugar beet cossettes are fed to the base of the tower. The towers are commonly 10 to 15 m high; different capacities are achieved by variations in tower diameter. In either form of construction, power consumption for a 5.5 m diameter tower (capacity: 3000 metric tons of beets per day) is about 40 kW [181].

The DE DANSKE SUKKERFABRIKER (DDS) diffuser extractor (Figure 8) may be regarded as a tower extractor with its axis turned about 80 deg. The extractor is normally installed at a one-seventh slope, and a double screw in the housing is used to transport the solids. The operating temperature is reached by
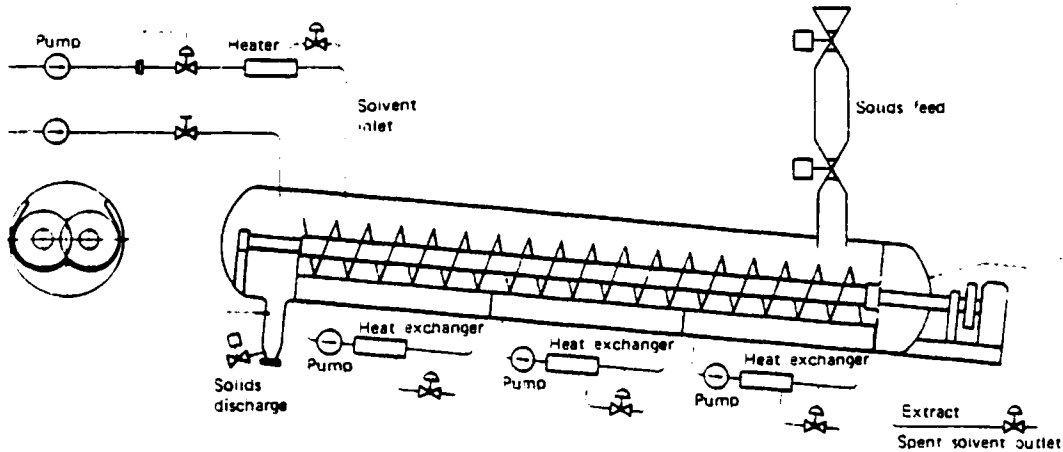
Figure 8.   DeDanske Sukkerfabriker (DDS) diffuser.   Courtesy of A/S Niro
            Atomizer [181].

employing jacket heating, thus avoiding the requirement for preheating. The

dimensions of the DDS diffuser and its power consumption are, broadly speaking,

similar to those of the tower extractors [181].

The use of these immersion extractors is contingent upon the ability to

transport solids without excessive back mixing. They need less space than

percolation extractors and lower power for the band drive and liquor circula-

tion [181].

The need to improve the desired product removal yield and to reduce the

contact time led researchers to introduce extra energy into the extraction pro-

cess. The most successful attempt seems to be the use of ultrasonic energy

along with immersion extraction. Using acetone as a primary extraction sol-

vent and heptachlor epoxide, contaminants were extracted in the laboratory with

ultrasonic waves; results were better than with the simple solvent extraction [94]. Ultrasonic energy was also used for removing the bitumen from tar sands with good results [164].

Soil-Related Experience

Removal of organic contaminants from soil is limited to laboratory techniques directed toward soil analysis rather than directed toward soil decontamination. Specific laboratory apparatus, such as SOXHLET and POLYTRON, is used; the extraction time is extended beyond any commercially acceptable period (e.g., 120 to 240 min). The ratio of the solvent to the soil is also unacceptably high (e.g., 1:1) [42].

Experiments with two nonmiscible solvents [i.e., polar (water) and nonpolar (kerosene)] have been successful in transferring the contaminant to the nonpolar solvent, but end up with high solvent content in the cleansed soil (e.g., 20 to 25 percent) [41]. All these experiments were conducted with high solvent-to-soil ratios.

GAS STRIPPING OF VOCs

Definition

To strip volatile organic compounds (VOCs) from soil, the VOC must be vaporized into a gas. The stripping may be done at essentially ambient temperatures, or heat may be expended to increase the rate of vaporization. Air or steam is the most likely stripping gas.

Process Parameters

- Heat--Although very little testing has been done in this area, the soil will have to be heated if VOCs are to be removed to acceptable levels by gas stripping. The soil will need to be heated to between 100 and 400°C, depending upon the vapor pressure of the VOC(s) to be removed and the adsorptive

forces binding the organic molecule to the soil particle. Depending on soil moisture, between 200,000 and 1,000,000 kJ/m^3 of soil treated will be required. The addition of recuperative heat exchangers will reduce the amount of fuel required.

• Stripping Gas—Gas flow can be accomplished by blowing the air through or over the soil under pressure or by using an induced-draft fan to pull the gas through the soil under a vacuum. Any gas may be used as the stripping agent. Practical considerations tend to limit the choice to air or steam. Which should be chosen will depend on the type of soil to be treated, the type of VOC to be removed, the site location, and the objectives of the procedure.

• Post-Treatment—Stripping of VOCs from soil with a gas at relatively low temperatures will produce a gas stream containing VOCs that must be removed or destroyed before the gas can be vented to the atmosphere. Removal of a condensible from a noncondensible by condensation is difficult and inefficient. For this reason, if the stripping agent is a gas such as air, removal and concentration of the VOCs by adsorption, or destruction by after-burning, appears to be the best choice. However, if the stripping medium is a condensible such as steam, condensation followed by an appropriate treatment procedure such as gravity separation, biological oxidation or adsorption, or a combination would appear to be the better choice. There are four air gas treatment options: a secondary combustion chamber, catalytic oxidation, gas scrubbing, and adsorption.

• Soil Preparation—Some form of feed pretreatment is required. Pretreatment may be merely prescreening to remove the large material such as boulders and logs. It is reasonable to assume that virtually all soils will contain fines that will be entrained in the gas. Provision must be made for the removal and adequate handling of these fines. Consideration must be given to the possibility that the VOCs may well be readsorbed on the surface of the fines if the gas is allowed to cool before the fines are removed.

• Soil Type—Silts and clays provide much more surface area per unit mass than sand and rock. In addition to a higher external surface area, some of this material may be porous, providing additional area and pores for adsorbing the VOC molecules. The wide range in particle size and density of most soils will provide severe problems for most stripping technologies and may well rule out the use of some. Soil high in clay will be particularly difficult to treat. Special provisions to prevent agglomeration and formation of clods will be required.

Equipment Unit Operation Description and Evaluation With Respect to Soil Cleaning

Equipment for above-ground removal of VOCs from soil by gas stripping consists of:

- Holo-Flite Screws or any similar technology

- Rotary kiln

- Hereschoff Furnace

- Circulating bed

- Bubbling bed

Holo-Flite Screw--

The Holo-Flite Screw is identified only because it was tested in this service; however any similar device would perform as well. Testing performed by R. F. Weston for the United States Army Toxic and Hazardous Materials Agency (USATHAMA) of the removal of VOCs from soil using a Holo-Flite Screw with induced airflow through the trough showed a removal efficiency of 99 percent [200]. Reported process conditions are:

Soil Discharge Temperature	50 to 150°C
Soil Residence Time	30 to 90 minutes
Air Inlet Temperature	Ambient to 90°C
Circulating Oil Temperature	100 to 300°C

Based on the reported test results, this technology appears to provide more than adequate removal and merits additional investigation.

- Advantages--

  - Mobile units are available.

- The units can be designed for energy efficiency because of the good contact between the soil and the flights and the relatively low gas flow rate.

- The low gas flow rate should reduce the cost of gas treatment facilities.

- Reported soil temperatures are moderate, which should further reduce processing costs.

- The unit should be capable of processing all types of soil. Soils high in clay could be a problem, requiring the addition of gravel that would be removed by screening after treatment and recycled.

● Disadvantages--

- The size of the equipment and the long holding times will limit throughput, possibly limiting the size of a site applicable to the technology and increasing unit processing cost, particularly labor costs.

Rotary Kiln--

A rotary kiln is normally used in waste processing as an incinerator. However, if the purpose is to remove VOCs without destroying the character of the soil or to operate at lower temperatures to avoid fouling, the temperature in the kiln can be controlled to between 100 and 400°C.

Contaminated Land Reclamation and Treatment (Appendix F) describes the cleaning of 5000 tons of soil in The Netherlands contaminated with hydrocarbons, using a two-stage rotating drum evaporator [134]. Ecotechniels has developed a full-scale system for heating the soil to 200 to 300°C and releasing the burned vapors in an after-burner at 800°C.

The rotary kiln thermal treatment to removal contaminants from soil by evaporation uses direct or indirect heat transfer to the soil. Direct heat

transfer requires large volumes of gas (1 to 2 m^3/kg soil) to provide the energy for raising the temperature of the soil. Indirect heating requires one-third less hot combustion gas.

- Advantages--

  - Can be designed to be mobile.

  - Can process any type of soil, but special processing is required for soils with a high proportion of clay.

  - With indirect heat transfer, the airflow can be relatively low.

- Disadvantages--

  - With direct heat transfer, the gas flow will be high, requiring expensive gas treatment facilities.

  - With indirect heat transfer, a very large heat-transfer surface (rotary kiln drum) is required.

  - Unless extensive heat conservation is provided, the process will expend large amounts of heat energy.

  - Rotary kilns are difficult to seal. Since the contaminants are not destroyed in the kiln, it must be operated at negative pressure.

  - Soils containing a high concentration of fines may not be suitable for processing, because prevention of fines entrainment is impossible.

The Hereschoff Furnace--

The Hereschoff furnace is a proven technology used in drying clays and regenerating activated carbon and other solids. To prevent binding and possible breakage of the flights, feed pretreatment to reduce the particle size is required. The pretreated soil, fed in at low temperature and containing water as well as contaminants, is fed to the center of the top tray, is gradually moved by the rotating flights to the outer edge, and falls to the second tray. These

rotating flights gradually move it to the center, where it falls to the third tray. Access ports are provided on each tray.

The process is repeated with the soil moving back and forth on the trays, falling off the bottom tray of the furnace, and being transferred to disposal. Fired heaters produce hot gases that are introduced into the furnace under the trays. For flexibility, many entrance ports are provided. The point for introducing the hot gases is optional, as is the number of trays. Trays below the point where the hot flue gas is introduced can be used for cooling the soil by introducing air at ambient temperature.

The gas moves countercurrent to the soil, and the flights cause the soil to roll as it is moved, thus exposing new surfaces to the gas.

Special precautions are needed when using this technology for treatment of soil containing hazardous VOCs. The unit must be air tight or operate under a slight vacuum. The gas is moved through the unit by an induced-draft fan. The type of gas treatment facilities to be provided depends on the contaminants removed and may not be needed in some cases.

● Advantages--

- Temperatures to 500°C are attainable.

- With a sufficient number of trays and proper operation, a reasonable energy efficiency is attainable.

- It is a demonstrated technology. However, whether it has been used to strip VOCs from soils is not known. It is used to burn hydrocarbons from clay.

- With reasonable pretreatment, all soils can be processed.

- Disadvantages--

    --A transportable unit capable of treating a reasonable amount of soil would
      be difficult to design.

    --Many trays would be required to achieve energy efficiency.

Circulating Bed Combustor--

The circulating bed combustor was developed for the combustion of high-sulfur fuel to produce steam. It was developed as a modification of the bubbling fluidized bed combustor because of fuel fines carryover. Fuel fines are recycled by a cyclone in the circulating bed. The technology should be applicable to stripping VOCs from soil with a gas. The reasons for the application of this technology would be removal of VOCs without substantially changing the character of the soil and the ability to handle soil fines.

Some slight modification is needed if this technology is to be used for stripping VOCs from soil. The incoming gas is preheated sufficiently to heat the soil to the required temperature and then passed through the distributor at a velocity sufficient to entrain the soil. Contaminated soil is added above the distributor, entrained and heated by the hot gas, removed by the separator, and returned for recycle. Treated soil is continuously removed from the separator. The number of cycles made by the soil is controlled by the soil inventory. The cleaned soil is cooled by heating the fluidizing air.

- Advantages--

    - The bed temperature and the holding time can be precisely controlled.

    - With proper pretreatment, relatively high-clay soil can be easily processed.

● <u>Disadvantages</u>--

- Expensive gas treatment facilities are needed to handle the large volumes of gas necessary to entrain the soil and to transfer sufficient heat energy.

Bubbling Bed Combustor--

A bubbling bed is made of a granular material (sandy soil) through which a gas is blown from a distributor at the bottom of the bed. The gas rate is controlled so that the bed material bubbles just to the point of incipient fluidization, but not sufficiently to lift solids from the bed. This technology can be used to remove VOCs from sandy soil by preheating the gas sufficiently to raise the temperature of the bed material so that the VOCs adsorbed on the solids are vaporized. The contaminated soil, which becomes the bed material, is fed in at the top of the bed and is withdrawn from the bottom (little back mixing of soil). The gas leaving the top of the bed is withdrawn from the free-board above the bed and appropriately treated before venting it to the atmo-sphere.

The residence time can be controlled by bed height and soil feed rate per bed cross-sectional area. The bed temperature is controlled by the temperature of the gas entering the bed.

● <u>Advantages</u>--

- Gas rate is lower than needed for a circulating bed, requiring less en-ergy and smaller off-gas treatment facilites.

- Solids separation and recycle facilities are not required.

● <u>Disadvantages</u>--

- Fines carryover requires additional fines treatment.

- The technology is limited to soils with very little range in particle size and density.

Section 4

CONCLUSIONS AND RECOMMENDATIONS

Above-ground extraction of organics and heavy metals is feasible from sandy soil containing very low levels of clay, silt, and humus. Above-ground extraction of organics and heavy metals from clay, silt, and humic soil fractions has not been demonstrated on the pilot plant scale. Separation of the extractant from the soil and regeneration of the extractant have not been successfully demonstrated for clay soils. Multiple extraction steps in series are required and severely compound the problem of recovering clean soil.

Contaminant extraction experience does provide enough information to support a decision on the feasibility of applying the technology at NPL sites. More applied research pilot scale testing must be conducted to support any statement on the technical, environmental, and economic practicability of extraction technologies. The development of innovative modifications to equipment to handle soils is hindered by the lack of a fundamental understanding of mobilization of the contaminant from the soil particle and regeneration of the extractant. Therefore, support for more research in this field should be directed at obtaining process parameters. Once the process parameters are known, cost estimates for NPL sites can be generated along with specific recommendations concerning the most economical and best environmental approach to be implemented.