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Technology Assessment of Currently Available and Developmental Techniques for Heavy Metals-Contaminated Soils Treatment

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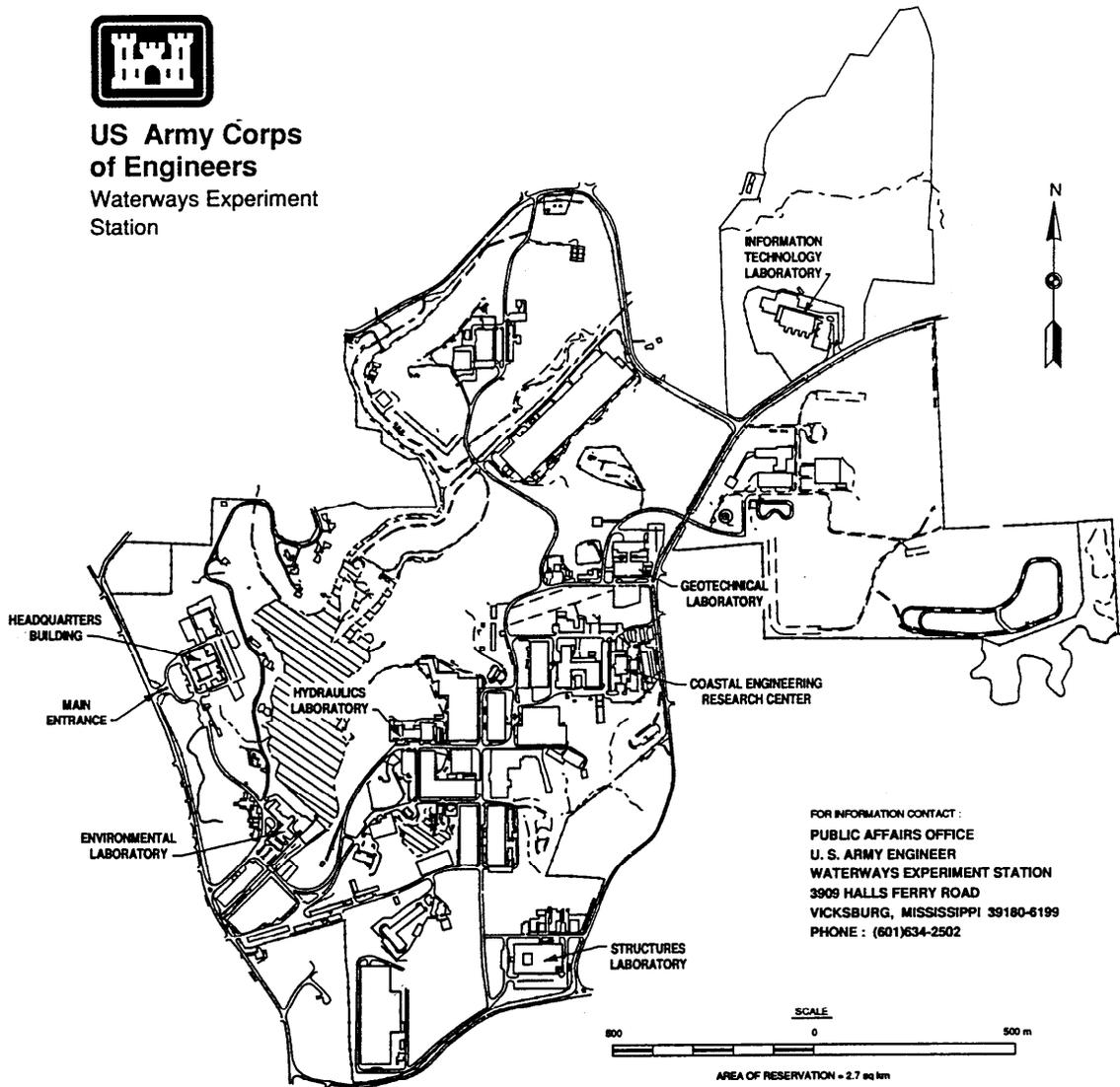
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Preface

The work reported herein was conducted by the U.S. Army Engineer Waterways Experiment Station (WES) as part of the Installation Restoration Research Program (IRRP) and the U.S. Army Environmental Quality Technology Research Program. This report is an extension of earlier work reported by Roy F. Weston, Inc., performed under Contract No. DAAK 11-85-D0007 for the U.S. Army Environmental Center.

Dr. Clem Meyer was the IRRP Coordinator at the Directorate of Research and Development, Headquarters, U.S. Army Corps of Engineers (HQUSACE). Dr. Bob York of the U.S. Army Environmental Center and Mr. Jim Baliff of the Environmental Restoration Division, Directorate of Military Programs, HQUSACE, served as the IRRP Overview Committee. Dr. John Cullinane, WES, was the IRRP Program Manager.

This report was prepared by Mr. R. Mark Bricka of the Environmental Restoration Branch (ERB), Environmental Laboratory (EL), WES, and Drs. Clint W. Williford and Larry W. Jones, under contract to the ERB. At the time of publication, Dr. Williford was employed by the Chemical Engineering Department, University of Mississippi, and Dr. Jones was employed by the Waste Management Research and Education Institute, University of Tennessee.

The work was conducted under the direct supervision of Mr. Norman R. Francingus, Chief, ERB, and under the general supervision of Dr. Raymond L. Montgomery, Chief, EED, and Dr. John Harrison, Director, EL.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Leonard G. Hassell, EN.

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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
cubic yards	0.7645549	cubic meters
Fahrenheit degrees	5/9	Celsius degrees or kelvins ¹
feet	0.3048	meters
gallons (U.S. liquid)	3.785412	cubic decimeters
gauss	0.0001	tesla
inches	2.54	centimeters
miles (U.S. statute)	1.609347	kilometers
pounds (mass)	0.4535924	kilograms
tons (metric)	1,000.0	kilograms
tons (2,000 pounds, mass)	907.1847	kilograms
watts per square inch	1,550.003	watts per square meter

¹ To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: $C = (5/9) (F - 32)$. To obtain Kelvin (K) readings, use: $K = (5/9) (F - 32) + 273.15$.

1 Introduction

Background

Past military and industrial activities have contaminated numerous U.S. Army installations with metals, solvents, and explosives. In response, the Army initiated the Installation Restoration Research Program in the early 1970s to address the cleanup of contaminated soil and groundwater that could impact the environment and restrict the use of Army land. The early stages of this program revealed the immense scope of the needed restoration effort at these sites. Many contaminants found at these sites were unique to the military.

Recently, the U.S. Army, Air Force, and Navy have divided responsibility for broad contaminant classes under a cooperative agreement based on the Reliance study. This agreement assigns the lead activity for research on heavy metals contamination to Army investigators. In support of this agreement, the Army, through the U.S. Army Engineer Waterways Experiment Station (WES), initiated research to develop more effective, economical, and environmentally responsible technologies for treating contaminated soils.

Metals contamination

Past military and industrial practices have led to several forms of heavy metal contamination. Typically, heavy metal contamination is found in the form of sludges, contaminated soils and debris, surface water and groundwater. Activities such as sand blasting, use of lead-based paints, and firing range operations have produced soils contaminated with discrete metal fragments or metallic smears on soil particles. Activities such as electroplating, metal working and refinishing, disposal of wastes in burning pits, munitions production, and cooling tower discharges have produced ionic forms of heavy metal contaminants that associate with soil particles.

Surveys conducted by WES and Roy F. Weston, Inc., indicate that the most frequently cited metal contaminants at military installations are lead, cadmium, and chromium. Mercury and arsenic occur to a lesser extent, but are of concern because of their extreme toxicity. As indicated by a database maintained

and operated by the U.S. Army Environmental Center (formerly the U.S. Army Toxic and Hazardous Materials Agency, USATHAMA), of the contaminants most frequently identified at Army installations, five are heavy metals (USATHAMA 1991). Of particular concern are abandoned firing ranges. Very high levels of lead are generally found in the berms and soils surrounding such areas, and remediation activities will be required.

The end of the Cold War will accelerate downsizing and closure of a number of military facilities. Simultaneously, the pressures to convert these properties to civilian purposes will grow more imperative. A number of facilities (e.g. Fort Ord) occupy properties with high economic value. Likewise, the U.S. Environmental Protection Agency (USEPA) continues to strengthen regulations regarding soil and water contamination. For example, a bill to strengthen the Clean Water Act (of 1972) is under consideration by the Senate and is expected to become law in 1992 or 1993. Regulatory requirements thus, will become more stringent and may also become clearer in terms of required action and treatment levels.

Unlike organic contaminants that can be destroyed (or mineralized) through treatment technologies, such as bioremediation or incineration, metal contaminants cannot. Once a metal has contaminated soil, it will remain a threat to the environment until it is removed or rendered immobile. Unfortunately, few technologies exist for the removal or immobilization of heavy metals. The cleanup techniques most used for the remediation of heavy metal contamination are excavation and subsequent landfilling of the heavy metal-contaminated soil or waste (commonly referred to as "dig and haul") or solidification/stabilization (S/S). Dig and haul does not remove the contaminant from the waste but simply transfers the contamination from one area to another. Usually, no effort is made to reduce the mobility of the heavy metals beyond containment in a secured landfill.

With implementation of regulatory criteria under the landban rules, the USEPA may require Best Demonstrated Available Technology prior to landfilling. S/S is one accepted approach. S/S treatment reduces the mobility of metals through chemical transformation and/or encapsulation. However, since metals (as elements) are not destroyed by chemical reaction, the underlying toxic agent remains in the treated material.

Study objective and scope

As a result of the growing concern regarding heavy metal contamination and the lack of metal treatment technologies available for remediation, an effort was initiated by WES to investigate possible treatment technologies for heavy metals. The purpose of this effort was to identify promising technologies--for the treatment of heavy metal-contaminated soils and for the resulting metal-contaminated residuals from such activities. Efforts were made to identify both immobilization and extraction technologies for contaminated soils. Recognizably, many extraction technologies produce metal-contaminated

aqueous side streams requiring treatment. In an attempt to be comprehensive, this discussion covers both solid and a limited number of aqueous phase metals treatment technologies.

This report presents a detailed discussion of the candidate technologies identified. Details regarding application to aboveground and in situ treatment, potential treatment effectiveness, long-term performance, residuals produced, adaptability to soils treatment, potential for scale up, and potential disqualifiers are discussed for each technology. Available cost estimates are cited.

This report does not present any information regarding the ranking or the recommendation of candidate technologies for future study. Such information will be presented in a subsequent report. Only the details of technologies that may have potential for the treatment of heavy metals-contaminated soils and resulting aqueous wastes are presented.

Report Organization

This report is divided into six chapters, as described below:

- a. *Introduction.* Provides background on heavy metals contamination at Army installations, the purpose and scope of this study, and the organization of the report.
- b. *Physical/chemical processes.* Describes and assesses processes that remove or immobilize metals in soil and water by application of chemicals, mechanical separations, or electrical potentials.
- c. *Thermal processes.* Describes and assesses processes in which the soil is heated to drive off or immobilize the heavy metals in soil.
- d. *Immobilization/stabilization/disposal processes.* Describes and assesses processes that immobilize the metals in the soil with cement like or polymeric compounds and/or isolate the contaminants in geological formations or constructed landfills.
- e. *Vegetative uptake.* Describes and assesses processes that remove metals from soil through plant root systems and concentrate the metals in the plant tissue.
- f. *Summary and conclusions.* Presents a concise summary and the major conclusions on the current practice of treating metals-contaminated soil and resulting aqueous streams, and the prospects and needs for alternative technologies.

Each technology review follows a consistent format, first providing a general description, diagrams, and assessment criteria. The process reviews are organized as follows:

- a. *Description.*
 - (1) Theory.
 - (2) Level of development.
 - (3) Available performance data.
 - (4) Conceptual design schematic.
- b. *Treatment effectiveness.* Actual or expected performance based on results available in the literature and/or engineering judgment. The treatment goal is to render the soils capable of passing the USEPA Toxicity Characteristics Leaching Procedure (TCLP) test for disposal as nonhazardous materials.
- c. *Long-term stability/performance.* Based on literature and/or engineering judgment, determine if treatment performance is likely to have permanent, long-term effectiveness in rendering the soil nonhazardous.
- d. *Residuals treatment/disposal requirements.* Identification of potential residual waste side streams (i.e., extract solutions) that will require further treatment and/or disposal due to expected hazardous properties.
- e. *Adaptability.* Ability to treat various soil/site types and other waste streams (i.e., sludges), to treat for organic compounds concurrently with metals, or to be readily linked to other processes for organic or explosive compound treatment.
- f. *Scale up potential.* Actual throughput rates and/or anticipated ability to scale up the process.
- g. *Potential disqualifiers.* Identify known or potential "fatal flaws" that could hinder development and implementation of the process, including
 - (1) Inherently unsafe.
 - (2) Uncontrollable environmental risk of mobilization.
 - (3) Uncontrollable air emissions.
 - (4) Exceedingly expensive.
 - (5) Exceedingly complex materials handling, operation, or maintenance.

2 Physical/Chemical Processes

Precipitation

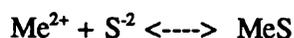
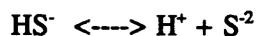
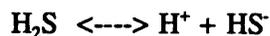
Precipitation is a process that converts a substance in solution to an insoluble form. This process alters the solubility of a metal species by reacting it with specific chemicals, causing it to "precipitate" from the solution. This approach may be adopted to soils to convert metals to insoluble species and reduce their mobility. Two general approaches exist: aboveground precipitation, in which soil is excavated and mixed with chemicals in process equipment, and in situ precipitation, in which chemical solutions are pumped into contaminated soil in place.

Aboveground precipitation

The aboveground precipitation process incorporates treatment chemicals with excavated soils using conventional mixing equipment. There is no published literature on the treatment of soils contaminated with metals (Lanouette 1977, Scott 1977, USEPA 1984b).

Several methods have been developed in the wastewater treatment field for precipitation of heavy metals from aqueous solutions, which might also successfully be applied to soils. The following is a brief description of some of the well-known methods.

Sulfide process. Heavy metals react with sulfide ions to form metal sulfides that are insoluble in water. The generic reactions for divalent heavy metal cations (Me^{2+}) can be characterized as follows (USEPA 1984c):



where "Me" is the metal ion.

Generally, as the pH of the solution increases, the solubility of the metal sulfide decreases. The amount of metal sulfide formed is dependent on the following:

- a. pH.
- b. Type of metal.
- c. Sulfide content.
- d. Other ions that interfere with the process.
- e. Soluble salt content of the waste.

In wastewater treatment, sodium sulfide (Na_2S) and sodium hydrosulfide (NaHS) are typically used as the sulfide source in the reduction reaction. However, sodium may adversely affect soil properties, particularly permeability (USEPA 1984c). This may be overcome in an aboveground "slurry" process, but may prevent effective in situ treatment.

It has been speculated that calcium or iron sulfide may be used. However, these have a low solubility in water and thus must be added as a slurry. While wastewater treatment with sulfides has been studied extensively, no experimental work has been done on treating soils. Therefore, no information is available for soils regarding the kinetics of the reactions, chemical loading rates, interfering reactions, etc.

Most metal sulfides are highly insoluble in water, with the exception of certain sulfide complexes formed by zinc, mercury, and silver, which are soluble in water.

The solubility of metal sulfides is lower across a wider pH range than all other precipitated species typically produced during wastewater treatment. However, a concern exists for more acidic soils to potentially produce hydrogen sulfide, which is a toxic gas. Since sulfide solubilities decrease somewhat with increasing pH (Figure 1), high soil pH may be more favorable for sulfide treatment. While no adjustment of alkalinity would be necessary for naturally alkaline soils, acidic soils may require lime addition to maintain a higher pH.

Under aerobic conditions, metal sulfides can be oxidized to form metal sulfates, which are more soluble in water, reduce pH, and thus tend to mobilize other metal ions. Aerobic or oxidizing conditions might be controlled by the incorporation of soil organic material and/or providing a surface barrier to water or air infiltration. However, susceptibility for metal remobilization remains a concern for long-term stability of treated soil.

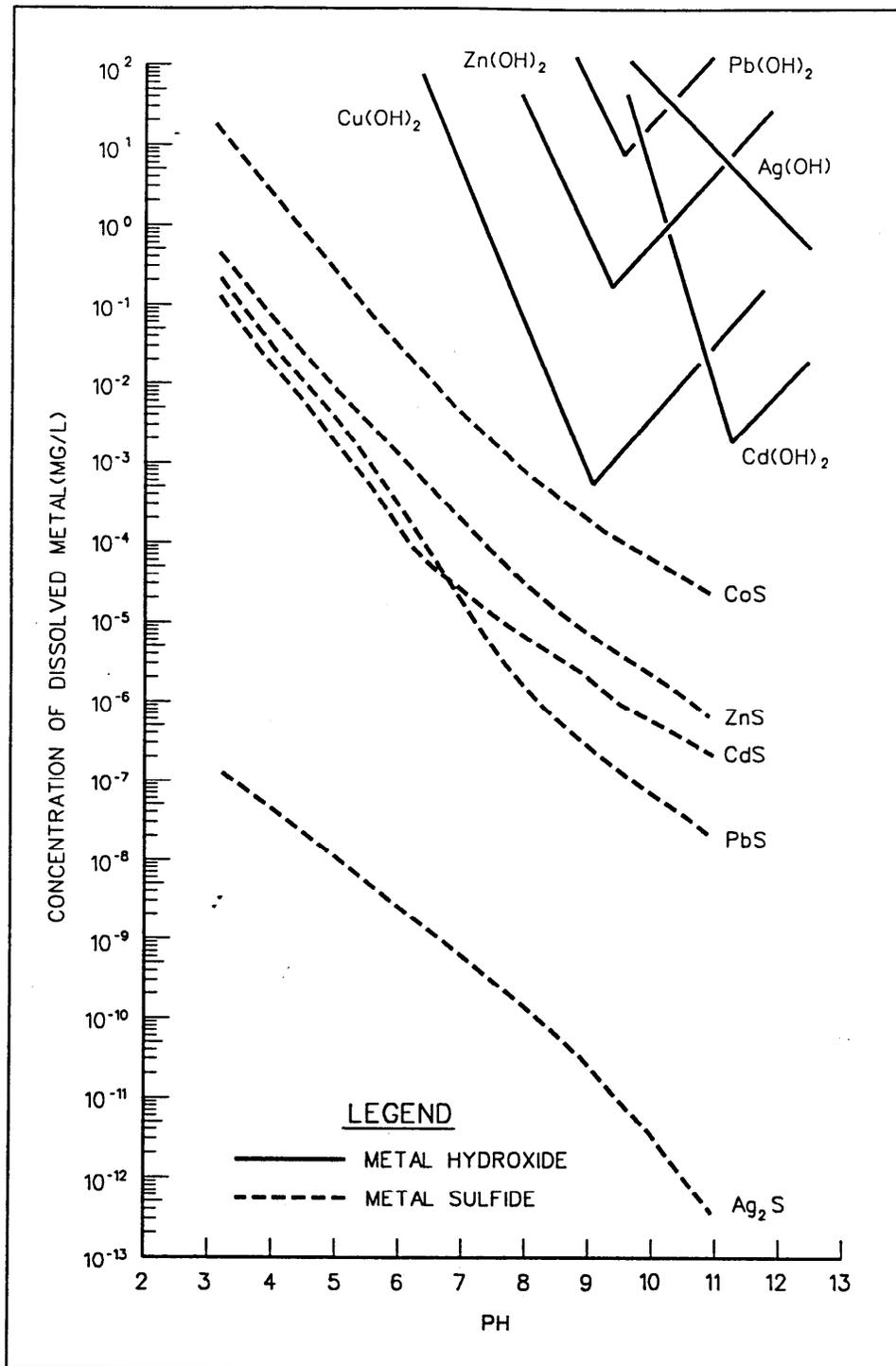


Figure 1. Solubilities of metal hydroxides and sulfides as a function of pH (after Freedman and Shannon 1973). (Note: plotted data for metal sulfides are based on experimental data listed in Seidell's Solubilities)

Sodium borohydride (NaBH_4) process. This process has been used in several chemical industry installations to treat metal-bearing wastewaters (Cushnie 1985). NaBH_4 is a strong reducing agent that can reduce many metal compounds to elemental metals. Where waste streams are contaminated with a single metal, the precipitate may be reprocessed or recycled for recovery of the metal. Where waste streams contain many metals, the advantage of this process over other precipitation techniques is the lower volume of sludge produced. However, this must be balanced against the higher costs of NaBH_4 .

The process involves adjusting the pH of the wastewater to between 8 and 11 and then adding NaBH_4 . The reaction time is approximately 30 min for complete metal reduction.

Again, there is no published literature on the applicability of this process to soils contaminated with heavy metals. NaBH_4 could be applied to the soil as a 98 percent powder or as a 12 percent solution mixed with caustic. The slow reaction rate observed for water may indicate a slower rate in soils. The reduction reaction products should remain stable in a reducing environment, but, as with sulfide precipitation, oxidation and remobilization may subsequently occur unless soil conditions are controlled. Depending on the nature of the metals in the soil, this concept may, upon further study, be applicable for the treatment of metal-contaminated soils.

One of the potential hazards associated with the use of this chemical is the evolution of hydrogen, a reaction product that is potentially explosive.

Cost information is available in the literature for the treatment of metals-contaminated wastewaters.¹

Starch and cellulose xanthate. This process was developed by the U.S. Department of Agriculture as a low-cost means of removing metals from wastewater (Wing and Rayford 1977). Figure 2 shows the typical process scheme.

The insoluble starch xanthate (ISX) acts as an ion-exchanger that rapidly removes heavy metal ions from wastewater, replacing them with Na^+ . ISX is mixed with wastewater and subsequently separated. Tests have shown that the process can operate in the pH range of 3 to 11, with greater effectiveness achieved at pH values >7.0 . Other advantages of this process include the fact that the ISX metal sludge settles quickly and dewateres easily. Experimental data have shown that the process can be operated in both the batch or continuous modes with significant metals removal being achieved. While the process is effective, ISX is thought to be too expensive relative to chemical

¹ G. C. Cushnie, Jr., P. Cranapton, and C. G. Roberts, 1983 (Dec), contract report prepared by Centec Corporation, Reston, VA, for U.S. Air Force Engineering and Services Laboratory, Tyndall Air Force Base, Florida.

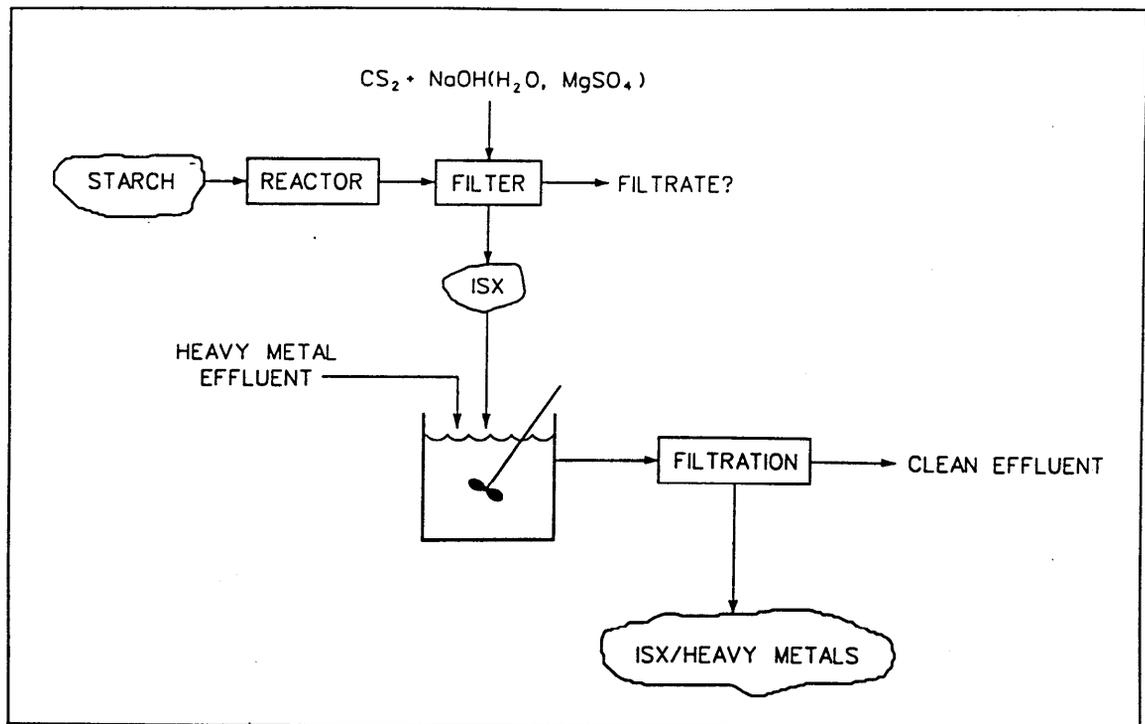


Figure 2. Production and use of insoluble starch xanthate for heavy metals removal from wastewater (from Wing and Rayford 1977)

precipitation at metal concentrations above 100 mg/L in wastewater (Wing and Rayford 1977).

There is no published literature on applications of this process to the treatment of metals-contaminated soil. Its successful application may be limited by the difficulty in distributing the insoluble starch throughout the soil and in its potential biodegradation in a biologically active soil.

Lime/carbonates/hydroxides processes. Heavy metal hydroxides and carbonates are only slightly soluble in water. This phenomenon has been used extensively to remove heavy metals from wastewaters. Metals are precipitated from solution as carbonates or hydroxides by adding hydrated lime. Control of pH is very critical in this process. Solubility curves for the metal hydroxides determine the best operating pH. Unlike sulfide precipitation, the solubility of hydroxides first decreases with increasing pH up to an optimum pH and then starts increasing again (Figure 1). Since the optimum pH varies widely between metals, all the metals in a mixture may not all be effectively treated by this method. This behavior is unlike that for sulfides, where the solubility continuously decreases with increasing pH.

Precipitation is followed by a sedimentation step where the metal precipitates are removed from the water by settling. Flocculating agents that improve the settling characteristics of the precipitate may also be added, prior to settling (Lanouette 1977, USEPA 1985).

This process has not been applied to the treatment of soils contaminated with metals. A study has been conducted applying lime as a barrier to migration of metals from municipal solid waste leachate to surrounding soils (Weston 1987). It was found that "breakthrough" of metals in a soil column was significantly prolonged when a layer of crushed limestone was utilized as a barrier, particularly for trivalent chromium. The results indicate that soil treatment to reduce mobility may be feasible. Since the solubility of hydroxides is sensitive to pH, applying this process to nonalkaline soils or in regions where the rainfall is acidic could result in long-term instability and potential remobilization.

Application to onsite soil treatment. While reduction, precipitation, and immobilization methods are well established for wastewater treatment, the earlier reviewers (Weston 1987) did not reveal their application for treatment of heavy metal-contaminated soil. Conceptually, an onsite soil treatment process would first involve excavating contaminated soil for input to process equipment. It could use either a slurry or dry mix process to distribute the treatment chemicals. A schematic diagram of a conceptual process appears in Figure 3.

The water slurry process could very effectively distribute both soluble treatment chemicals (e.g., sodium hydrosulfide) and insoluble chemicals (e.g., lime) throughout the soil. Slurry treatment with water may provide more rapid reaction of soluble metal species to form precipitates. The treated soil would require dewatering prior to backfill or landfill disposal.

A dry mixing process using large-scale solids mixing equipment (e.g., pug mill, screw mixer, etc.) would mix insoluble treatment chemicals with the soil. Reaction may occur at a lower rate since metals dissolved in the soil pore moisture or adsorbed onto soil surfaces may not be in contact with the treatment chemicals. The migration of metals to the chemical via percolation or the low-level dissolution of the chemical into the soil moisture could prevent migration of unreacted metals from the bulk soil mass.

Treatment effectiveness. The process concept, treatment chemicals, dosage, matrix effects, and pH require further study to determine if performance is acceptable for soil contaminant remediation. Leach test performance, although not the sole determinant, depends upon the selection of leaching the solution. Likewise, sample-air contact during leaching procedures may produce results unrealistic for field conditions. Sulfide precipitation achieves low solubility under a wider pH range, with the best performance probably with exposure to mild acids. Soil treated by this method would therefore tend to resist leaching of metals better than soil treated by hydroxide or carbonate precipitation methods. Use of the latter two methods may require additional and excessive alkaline material to maintain a high pH during performance of the TCLP extraction test.

Landfill performance is of more fundamental importance than leach test performance. Ultimately, preserving long-term performance after backfilling

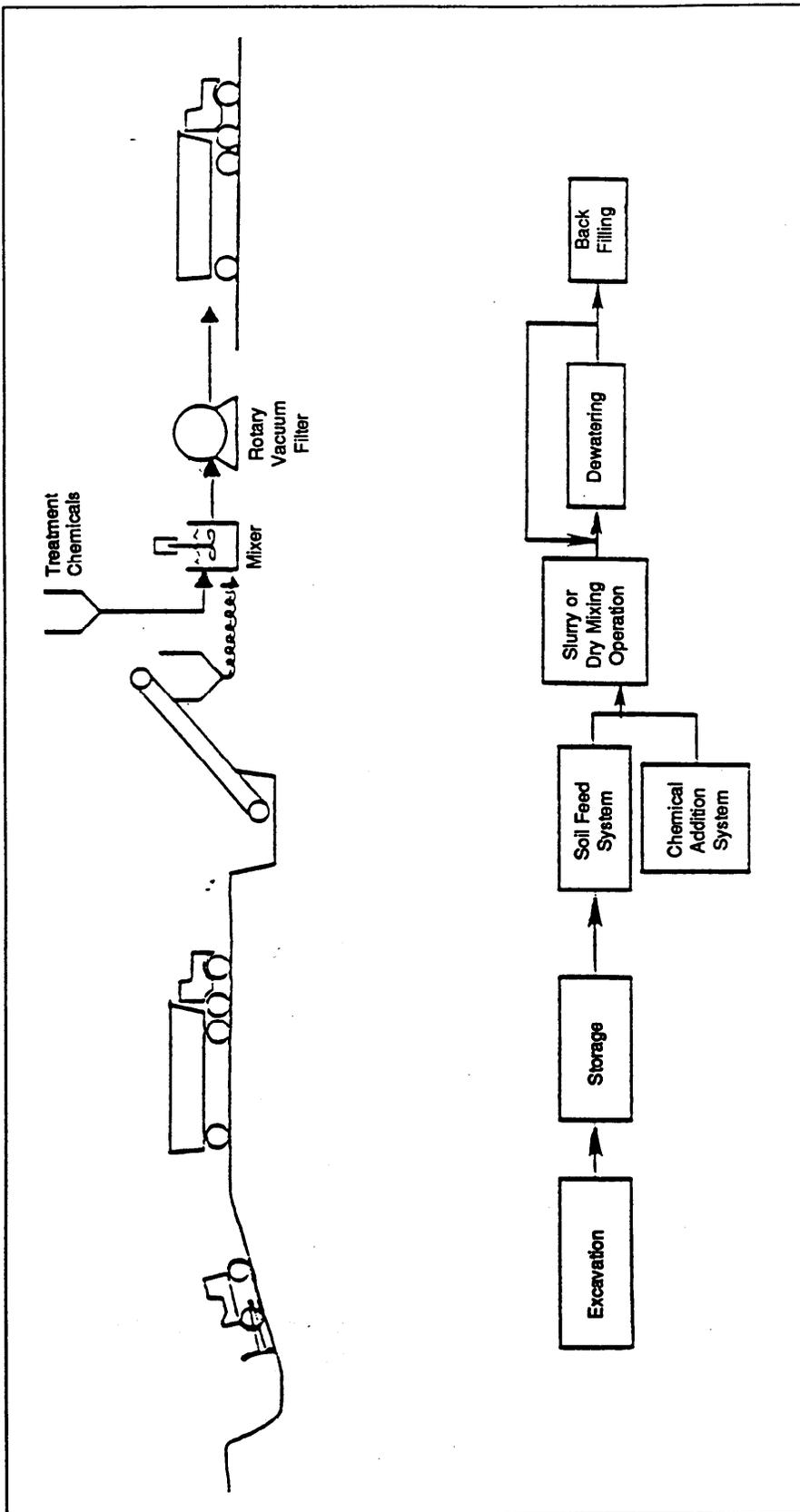


Figure 3. Aboveground precipitation; flow block diagram (from Weston 1987)

onsite or landfilling may require runoff controls and/or infiltration barriers to prevent exposure to destabilizing acidic or oxidizing agents.

Another option would be to use these processes in conjunction with extractive procedures. In this manner, metals could be first extracted into an aqueous phase and then precipitated out using the above processes. This is considered in the discussion of extraction technologies (see following section of Chapter 2, entitled Extraction).

Long-term stability/performance. Since there are no experimental data on the applicability of these processes to soils, comments on treatment stability and performance are based on engineering judgment. Soil properties such as pH, form of the metals, and oxidation-reduction potential will play a critical part in determining the long-term performance of the process. One of the problems already identified is the dependence of these processes on pH. This means that some arrangement for maintaining the pH level by liming, etc., would be required to prevent chemical resolubilization. For example, metal sulfides are susceptible to oxidation to water-soluble, acidic sulfates. Maintenance of a chemically and physically stable environment is essential to successful implementation of these precipitation technologies in terms of long-term performance.

Residuals treatment/disposal requirements. One of the biggest disadvantages of the above processes is that the metal precipitates and soil remain together and must be backfilled or disposed. Disposal requirements for the treated soil would depend on extract metal concentrations and anticipated long-term stability. Liquid effluents from the processes could be recycled, discharged, or may have to be treated prior to disposal depending on metals concentrations.

Adaptability. The process is clearly able to treat aqueous wastes containing metals. The process is designed to primarily address metals and is unlikely to effectively treat for organic compounds. While there are no experimental data to prove that these processes can be used to treat soils, if successful, they may also be applied to residues from organic soil treatment processes, including incinerator ash. Since sludges of interest already contain metal precipitates, further treatment may not be effective in altering sludge characteristics.

Scale up potential. The process may be scaled up using existing solids-handling and mixing equipment. Scale up should be readily achievable.

Potential disqualifiers. The principal concerns regarding application of the aboveground precipitation process are as follows:

- a. A lack of field application history. Application of precipitation to soils treatment is purely conceptual at this stage. Extensive research and development work is necessary to evaluate the feasibility of applying these processes to soils.

- b.* Depending on soil matrix and the nature/form of the metal contaminants, the kinetics of the processes would probably differ from those observed in wastewater treatment.
- c.* Chemical and handling costs could be considerably higher than those associated with wastewater treatment.
- d.* Another disqualification may be the instability of the precipitate. Under some environmental conditions (e.g., at lower pH values, oxidative environment), the precipitates may resolubilize. The use of sodium borohydride and sulfides may also present some safety risks because of the potential generation of hydrogen and hydrogen sulfide.

In situ precipitation

Description. The basic considerations for this process are the same as those described previously for aboveground precipitation. In this process, chemicals are directly applied to the soil to precipitate the metals and decrease their mobility. This discussion is limited to the application of precipitation in situ.

The four methods considered for in situ precipitation or reduction/precipitation of heavy metals are the same as those for aboveground precipitation, namely:

- a.* Sulfide process.
- b.* Sodium borohydride process.
- c.* Starch and cellulose xanthate process.
- d.* Lime/carbonates/hydroxides process.

The theory behind all these processes is discussed in the previous section on aboveground precipitation.

The application of these processes to soils contaminated with metals has not been studied in great detail. Most of the experience with these processes has been in the area of wastewater treatment. Heavy metals sometimes exist in soil as discrete fragments. Otherwise, they primarily exist at ion exchange sites or adsorbed onto various geochemical substrates, e.g. clays, organics, or hydrous iron and manganese oxides and hydroxides (Horowitz 1991). Extraction studies have shown that, given favorable reaction kinetics and thermodynamic driving force, weakly bound compounds can be mobilized from soil (Calmano and Forstner 1983). Conceptually, processes for treatment of metal-contaminated aqueous wastes should be applicable to heavy metal-contaminated soil. However, an excess of treatment chemicals may be

necessary to ensure complete reaction, because of competing soil ion exchange or precipitation reactions.

Given the variation in soil types, structures, etc., and the extent of the contamination, the applicability of these processes would be site-specific. Table 1 lists site and soil characteristics that are important with respect to in situ (and to some extent, aboveground) treatments. Heavy metals interact with soils and

Table 1 Site and Soil Characteristics Identified as Important in In Situ Treatment
Characteristics
Site location/topography
Slope of site-degree and aspect
Soil, type, and extent
Soil profile properties Depth Boundary characteristics Texture ¹ Amount and type of coarse fragments/grain-size distribution Structure ¹ Color Degree of mottling Presence of carbonates Bulk density ¹ Cation exchange capacity ¹ Clay content Type of clay pH ¹ Eh ¹ Surface area ¹ Organic matter content ¹ Nutrient status ¹ Microbial activity ¹
Hydraulic properties and conditions Depth to impermeable layer or bedrock Depth to groundwater ¹ (including seasonal variations) Infiltration rates ¹ Permeability ¹ (under saturated and a range of unsaturated conditions) Water-holding capacity ¹ Soil water characteristic curve Field capacity/permanent wilting point Flooding frequency Runoff potential ¹ Aeration status ¹
Climatological factors Temperature ¹ Wind velocities, directions, and ranges--seasonal and diurnal
Source: Weston 1987. ¹ Factors that can be managed to enhance soil treatment (source: Sims and Wagner 1983).

usually accumulate in natural systems near the surface. Downward transport will depend upon the factors listed, particularly as they affect metal compound solubility, soil-metal interaction, and soil permeability. For instance, metal solubility and thus mobility are generally enhanced in acidic soils, where the buffering capacity has been exceeded. Figure 4 shows the various phenomena that influence soil metal concentrations.

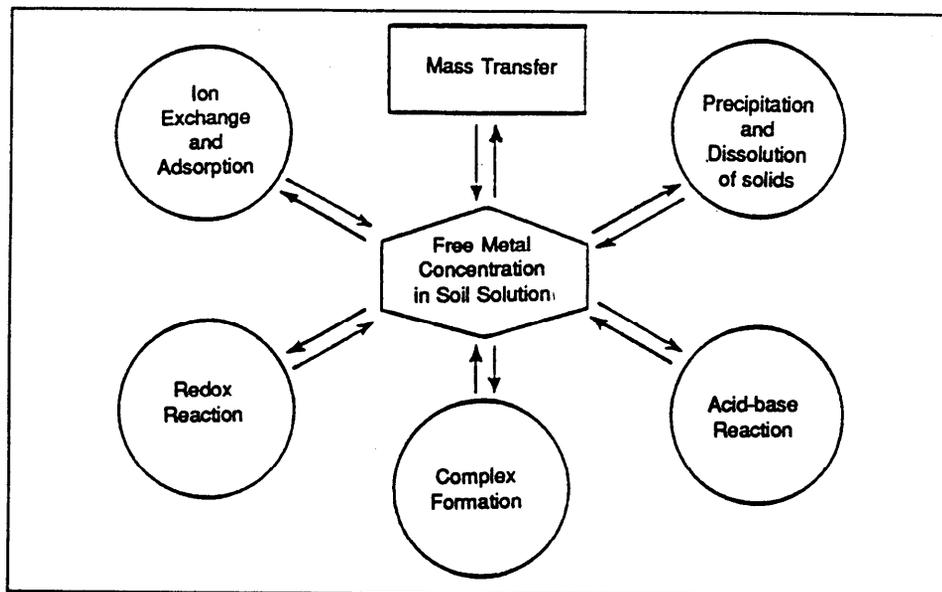


Figure 4. Phenomena that influence soil metal concentrations (after Mattigod, Sposito, and Page 1981)

The soluble treatment chemicals for in situ processing could potentially be applied as chemical solutions (e.g., sodium sulfide) and allowed to percolate through the soil to the required depth. Other chemicals (e.g., lime, sodium borohydride) must be applied as a slurry or solid and incorporated into the soil by tilling.

Liquid applications should employ surface controls, diking, and grading to prevent unwanted surface runoff of chemicals and migration of excess chemicals to the groundwater. Doses can be determined by laboratory and pilot testing. Chemical dilution may be necessary to ensure adequate percolation to the desired treatment depth. These measures may result in excess reactants migrating into the groundwater. Although soluble sulfides, carbonates, and hydroxides are not highly toxic in trace quantities, groundwater recovery and treatment or reapplication may be necessary, depending on site hydrogeology, groundwater use, and regulatory constraints.

Following liquid application, additional measures to control the soil environment may be necessary to improve the long-term performance of the remedial action. Limestone applied in large doses and tilled into the soil could supply a large buffer capacity to protect against soil acidification. Measures to prevent oxidation of reduction/precipitation products may include capping or

application of natural organic matter that, as it decomposes, maintains a reducing environment.

The application of slurry or solid chemicals by spreading and tilling would lessen the need for special runoff and runoff control measures such as grading and diking, since the chemicals have been incorporated into the soil. In fact, limited irrigation may be desirable to consolidate the soil and encourage downward movement and contact of the reactants with the metals. This type of application process may be limited in its effectiveness for treatment of contaminants well below the ground surface.

A more intensive application procedure for solid or slurry reactants might include mixing at depth using heavy excavating and earth-moving equipment. These methods would result in performance and costs between that of onsite precipitation (excavation and mixing process equipment) and surface application.

Following successful reduction/precipitation, posttreatment measures for surface application methods, as described above for liquid application methods, may be beneficial in maintaining performance over the long term.

Treatment effectiveness. As in the case of aboveground precipitation, the effectiveness of these processes in treating metals-contaminated soils has not been established. However, based on the soil matrix and the experiences from wastewater treatment, these processes can be effectively used to immobilize metals in soil. Since applicability of these processes is site specific, laboratory tests on the particular soil must be done to select treatment chemicals, dosage, soil pH, mixing requirements, moisture content and reaction time and to assess performance. Treated soil should be further studied to determine the effects of environmental stresses (pH, oxidation) on metals leachability. In addition, pilot studies must be conducted before applying the full-scale process to field situations.

Long-term stability/performance. Since the applicability of these processes to soils contaminated with metals has not been demonstrated, estimates on long-term precipitate stability and performance are based on engineering judgment. In the long term, changing soil pH and oxidation of reduction/precipitation products could potentially destabilize, i.e. resolubilize, metal contaminants. This is problematic for long-term stability. The impact of these conditions on stability should be studied in the laboratory and, subsequently, on demonstration sites. With additional treatment or site controls that can be used to maintain soil pH and a reducing environment, precipitation could be an effective means of immobilizing metals in soil. Of course, long-term reliability will be lower than for technologies that remove the metals. This suggests that in situ precipitation may best be applied to sites with low-level contamination or with low risk of migration and exposure. Alternatively, in situ precipitation could be combined with established approaches for low-risk sites, such as capping, to provide secondary protection against migration.

Residuals treatment/disposal requirements. Application of any of the above processes to soils contaminated with metals will result in a mixture of soil and immobile metal precipitates. Therefore, presumably there would be no residual soil "disposal" requirements. Depending on how the chemicals are applied to the site (e.g., solution slurry or solid form), it is possible that a liquid effluent may be generated (runoff, or groundwater recovery) and require recycling or treatment. These potential requirements would be determined in the testing and development phase, but are not considered significant obstacles to implementation.

Adaptability. The ability of these processes to treat heavy metal-contaminated aqueous wastes has been well established. Sites with combinations of organic and metal waste contamination may be difficult to treat because of the potential for the formation of water-soluble organometallic complexes. The formation of soluble complexes might also result from the organic matter added to maintain reducing conditions. The precipitation reaction would have to form thermodynamically stable precipitates relative to soluble complexes to prevent resolubilization. Finally, these precipitation processes have relatively little effect on organic contaminants. For this reason, these processes are not effective for the treatment of soils contaminated with organics.

Scale up potential. In situ precipitation may use typical farm fertilizer application or spray application techniques to rapidly treat contaminated soils. Established runoff/runoff or groundwater control techniques are also available and readily implementable. Scale up should be achievable, and rates of treatment should far exceed those for aboveground precipitation techniques. These advantages would probably facilitate regulatory acceptance.

Potential disqualifiers. The principal concerns regarding the application of in situ precipitation are as follows:

- a.* Of great concern is that the applicability of these processes to contaminated soils has not been demonstrated.
- b.* Another significant uncertainty is the stability of the precipitates with regard to pH or oxidation-reduction potential.
- c.* Treatment of heavy metal contamination well below surface level would require development of injection methods.
- d.* Other issues include the need for long-term monitoring, the risk of migration of the treatment chemicals and safety hazards associated with sulfide treatment chemicals (H_2S release under acidic conditions) and sodium borohydride (H_2 release from reaction).

In situ precipitation by vapor phase application

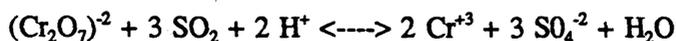
Description. This recently developed technology includes the vapor phase addition of sulfur dioxide (SO₂) for chromium reduction and the addition of sulfides (as iron sulfide or other sulfide salts) for the removal or immobilization of most heavy metals as metal sulfides.

Gas phase introduction of SO₂ and/or hydrogen sulfide (H₂S) has some advantages over liquid chemical addition. The gas can be more rapidly distributed because of low viscosity and may more readily overcome barriers to liquid percolation.

Gas would be circulated via input and withdrawal wells screened in the unsaturated contaminated soil zone. Because of the hazardous properties and high mobility of the gases, precautions must be taken in system design to prevent the release of gases. Withdrawal wells operate at a vacuum, and input wells operate as vacuum breakers, near atmospheric pressure. Since the soil system as a whole will be exposed to a vacuum, the soil surface will be sealed to reduce infiltration. Soil sealing may be accomplished by applying a bentonite slurry or asphaltic sealer, or by capping with impermeable plastic sheeting.

SO₂ or H₂S will be absorbed into the soil moisture or adsorbed onto the soil. Neutralization, reduction, or precipitation reactions are then completed in situ. These chemical reactions are widely used in wastewater treatment for metals removal and were discussed in the subsection entitled Aboveground precipitation (page 5).

The reaction for SO₂ reduction of hexavalent (Cr⁺⁶) has been described as follows (Campbell et al. 1977).



The anticipated reaction for H₂S precipitation of divalent metal cations was given in the discussion of aboveground precipitation (see page 5).

The H₂S precipitation process results in a net addition of acidity to the soil, necessitating higher initial soil alkalinity or soil additives to increase alkalinity. While metal sulfides have a low solubility across a wide pH range, metal sulfide solubility increases as pH declines. Low pH will also result in lower H₂S solubility because of the solution equilibrium with sodium sulfide (Na₂S) and calcium sulfide (CaS).

The gas can be recycled with the periodic addition of H₂S and SO₂ to maintain target levels. Some excess gas will accumulate as a result of net gas leakage into the system. This will require gas treatment prior to discharge to the atmosphere.

In addition to rapid, even distribution of the reactants, this mode of chemical addition can result in less excess chemical addition to the groundwater and soil as compared with liquid phase application. Its principal disadvantages are the safety hazard that could result from the release of gases, particularly the highly toxic H_2S , and in the ability to ensure complete coverage.

Treatment effectiveness. This technology is presently in its early conceptual stage. Performance is likely to be comparable to in situ precipitation. The effectiveness of vapor phase application depends on reactant solubilities, moisture content, and alkalinity in the soil.

Long-term stability/performance. Since there are no experimental data on the applicability of these processes to soils, comments on treatment stability and performance are based on best engineering judgment. Soil properties such as pH, form of the metals, and oxidation-reduction potential will play a critical part in determining the long-term performance of the process. With metal sulfides, the most critical concern is chemical conversion to more soluble species. Under oxidizing conditions, the possibility exists for conversion to water-soluble sulfates. This might be prevented by incorporating organic matter into the soil and/or surface infiltration controls, but long-term performance is clearly a key concern in successful use of this technology. Note the previously cited concern about the generation of water-soluble organometallic complexes as the organic matter decomposes.

Residuals treatment/disposal requirements. Application of this process will result in immobile metal precipitates remaining in the soil. Therefore, no residual soil disposal is required. The excess air extracted from the system necessary to maintain vacuum on the soil may contain residual SO_2 or H_2S . This air stream will require treatment before discharge to the atmosphere. Caustic scrubbing should be effective and may allow for subsequent regeneration of H_2S for reuse. Some absorption of these gases into the groundwater may occur, which could result in migration of contaminated groundwater from the site. Although these compounds will tend to oxidize over time to the less hazardous constituents, groundwater management may be necessary where groundwater users could be impacted.

Adaptability. Volatile organic compounds (VOCs) have been successfully treated using in situ volatilization techniques in pilot and full-scale operations. This technology uses the same gas-moving processes and potentially offers simultaneous application of reactants for metals precipitation and removal of VOCs. The excess air stream could be treated for reactants and vented or treated for VOCs. Air venting rates have not yet been established for in situ precipitation, so the compatibility of the two is not certain. Adjustments to reactant concentrations may be made, however, to match the requirements for metals precipitation and VOC removal.

Concentrated sludges are typically composed of insoluble precipitates and would not derive additional benefit from this treatment. Since incineration

residues and low-temperature thermal treatment residues are often available onsite, in situ methods may not be advantageous.

Scale up potential. The in situ gas treatment system can be installed over large land areas for treatment of the unsaturated soil. The rate of treatment has not been established, but is expected to exceed the rates for aboveground precipitation techniques.

Potential disqualifiers. The principal concerns regarding the use of in situ precipitation by vapor phase application are as follows:

- a. The single largest concern is the unplanned release of toxic gases. While the system is designed to operate largely under vacuum, the reactant, particularly H_2S , presents a significant employee safety hazard and possible adverse public reaction to odors.
- b. Treatment effectiveness (both short and long term) have not been demonstrated.
- c. Other potential disqualifiers shared with liquid or slurry-based precipitation are the uncertain stability under long-term oxidizing conditions. As a result, there is a need for long-term monitoring and a need to assess the migration of chemicals used for treatment.

Extraction

Aboveground extraction

Description. In this process, contaminants are removed from the soil by one or more extraction solutions. The mechanisms for contaminant transfer to the solution phase include solubility, formation of an emulsion or soluble chelation product, and chemical reaction (USEPA 1985). For metal extraction, reaction by acidification and/or chelation is the predominant mechanism used.

This process involves excavation of the soil and treatment with one or more chemical wash solutions to remove metals. The wash solution (containing the extracted contaminants) is further treated to remove the contaminants, and the clean solution is recycled to treat additional soil or discharged. The number of washes, soil/solution ratios, and other process requirements are determined by site-specific conditions such as soil type, metals present, metal species, etc.

Solvent extraction is used extensively in the chemical processing and metallurgical industries. In the latter industry, extensive work has been done on the recovery of metals from ore as well as waste from metallurgical operations. Extensive study has been done using an extraction process for treating metal-plating wastewater followed by selective recovery by precipitation and/or extraction. There is a strong incentive for metallurgical and plating industries

to find methods to treat their metal-bearing wastes since disposal costs are high and valuable metals are being lost.

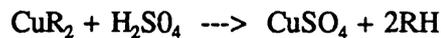
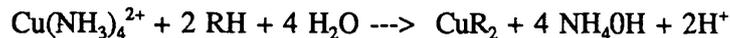
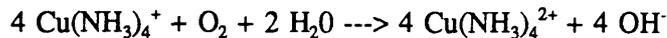
Recent literature is available on the applicability of this process to metal-contaminated soils (Oliver and Carey 1976; USEPA 1980; Lo, Baird, and Hanson 1983; Yamamoto 1984; Connick, Blanc, and O'Shaughnessy 1985; USATHAMA 1985; Ellis, Fogg, and Tafuri 1986; Castle et al., undated). Investigations range from experimental to field applications. Several solutions/methods have been studied to extract metals from soils. The following are brief descriptions of these methods.

- a. *Acids/NH₃*. Both strong and weak acid solutions have been used in the metallurgical industry to extract metals. Acid solutions dissolve basic metal salts such as hydroxides, oxides, and carbonates. Using strong acid solutions to treat soils may present problems because of the potential hazardous residues left in the soil or alterations of soil physical properties. Soils with sufficient alkalinity to buffer acids may be treated with a dilute solution of a strong acid such as sulfuric acid (H₂SO₄); otherwise, weak acids such as acetic acid may be preferred. In one experiment, municipal sludge was treated with H₂SO₄ to extract a whole range of heavy metals (USEPA 1980). With the exception of lead (Pb), all the heavy metals (Fe, Al, Zn, Mg, Ca, Ni, Ar, Cr, and Mn) were extracted to some degree by H₂SO₄. The extracted solution was then treated with lime to alter the pH and precipitate the metals. A similar acid extraction process has been proposed by the U.S. Army Environmental Center for treatment of plating sludge, with selective precipitation and extraction for metal recovery. Recovery of metals is less cost effective at lower concentrations, especially when there is a mixture of metals.

Bases, like acids, may also be used in certain treatment processes. In an experiment on recovery of metals from electroplating of sludge incineration residue, metals were first extracted by using H₂SO₄ and then precipitated by using sodium hydroxide (NaOH). However, the presence of large quantities of iron in the precipitate created problems. The precipitate was then treated with ammonium hydroxide (NH₄OH) to solubilize all metals except iron (Oliver and Carey 1976).

Material and handling costs would be slightly higher for this process compared with other extraction processes because of the corrosive nature of the acids and bases. Subsequent treatment of the extract will depend upon type and number of the metals present in the soil. Some of the studies directed toward recovery have shown that the process may only be cost effective for large-scale plants.

Copper has been recovered from scrap steel by ammonia leaching and solvent extraction. The basic reactions are as follows (Lo, Baird, and Hanson 1983):



There are similar processes for recovery of heavy metals from solid wastes (Lo, Baird, and Hanson 1983).

- b. *EDTA/hydroxylamine/citrate/water.* EDTA (ethylene-diamine-tetracetic acid) is a chelating agent that forms a metal-chelate complex when reacted with metals. These complexes are resistant to decomposition and degradation and can be used as a means of extracting metals from soil. Other chemical agents include citric acid and diethylene-triamine-pentacetic acid.

Upon reacting with metals, these agents form complexes that are soluble in water. The extract is treated to concentrate or recover the metals. The chelating agent should be recycled for cost-effective treatment.

In some soils, metals are strongly adsorbed by the magnesium and iron oxides in the soil, and extraction with only a chelating agent is insufficient. In such instances, the metal oxides are first reduced and then mobilized into solution. This is accomplished by adding treatment agents such as hydroxylamine and sodium dithionite/citrate along with EDTA (USEPA 1985).

Ellis, Fogg, and Tafuri (1986) have demonstrated that a sequential treatment of soil (from an actual Superfund site) with EDTA, hydroxylamine hydrochloride, and citrate buffer results in the following metal removal efficiencies: cadmium - 98 percent, lead - 96 percent, copper - 73 percent, and nickel - 23 percent. Similarly, Connick, Blanc, and O'Shaughnessy (1985), in an experiment on soil from another Superfund site, showed that water with EDTA is the most effective reagent for removal of metals. One of their observations was that using water/EDTA/buffer solutions resulted in the formation of precipitates with a resultant decrease in permeability. Finally, work reported by Castle et al. (undated) and in related unpublished work shows that EDTA rinse solutions are effective in removing lead only when the soil concentrations are low.

- c. *Other extraction processes.* In some instances, contaminants can be extracted from soil using water alone. Most of the lower molecular weight hydrocarbons can be extracted from the soil with water. Water-soluble inorganic salts such as carbonates can also be extracted with water (USEPA 1985). For metals, a full-scale project has been

successfully implemented by the Navy to clean up soil contaminated with chromic acid at Pearl Harbor, Hawaii (Yamamoto 1984).

Other extraction chemicals (for reaction/chelation) remain unexplored which could have potential application for specific metal species and soil characteristics. These can be used as a single treatment step or in combination with other chemicals.

Numerous techniques are available for the removal of metals from solution. These should be carefully selected to achieve maximum chemical use/reuse and to minimize the hazardous properties and volume of residues.

- d. *Aboveground extraction process.* The use of chelating agents and other additives in removing metals from contaminated soils has been clearly demonstrated at the laboratory level. Many of these tests were done with an intent of evaluating their use for in situ extraction. However, these results are also directly applicable to aboveground extraction.

The process can take many potential configurations, ranging from simple batch immersion to continuous multistage processing. The Navy performed a simple batch, water-wash treatment for about 2,200 cu yd¹ of chromic acid-contaminated soil. The washing or "extraction" equipment was essentially a 2-cu yd hopper modified with a port at the bottom. The soil was repeatedly washed with water to extract chromium. The extract was subsequently chemically treated to meet discharge standards. The sludge generated by the treatment of the extract was disposed in a hazardous waste landfill while the treated soil was disposed in a conventional landfill because it was rendered nonhazardous. The process for soil and extract treatment is shown in Figure 5.

A more complex continuous process was implemented for the cleanup of lead-contaminated soil at a Superfund site, as discussed above. A preliminary flowsheet for this process is shown as Figure 6. The continuous process offers the potential advantage of higher treatment capacity. Disadvantages include difficulties in material handling for soils that may contain rocks and debris, higher solution volume requirements, and more difficult process control for ensuring complete treatment.

Treatment effectiveness. Removal efficiencies vary with the type of metal, soil characteristics, choice of reagents, etc. Literature seems to indicate that the process is very effective in removing certain metals and ineffective for other metals. Generally, lead seems to be less susceptible to acid leaching, and chromium and nickel appear to be less susceptible to EDTA extraction. In addition, the level of cleanup necessary (e.g., TCLP or human health criteria)

¹ A table of factors for converting non-SI to SI units of measurement is presented on page vii.

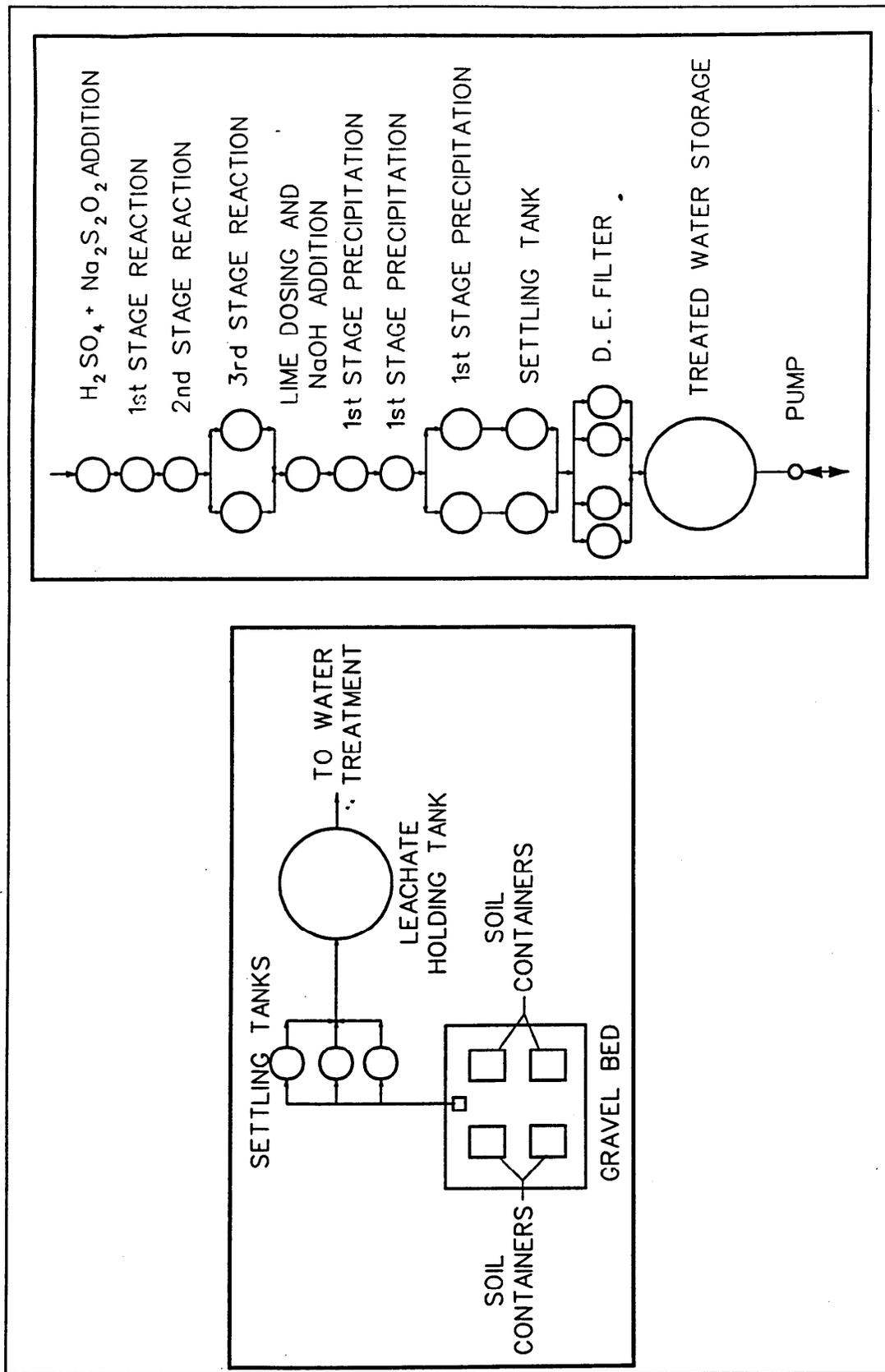
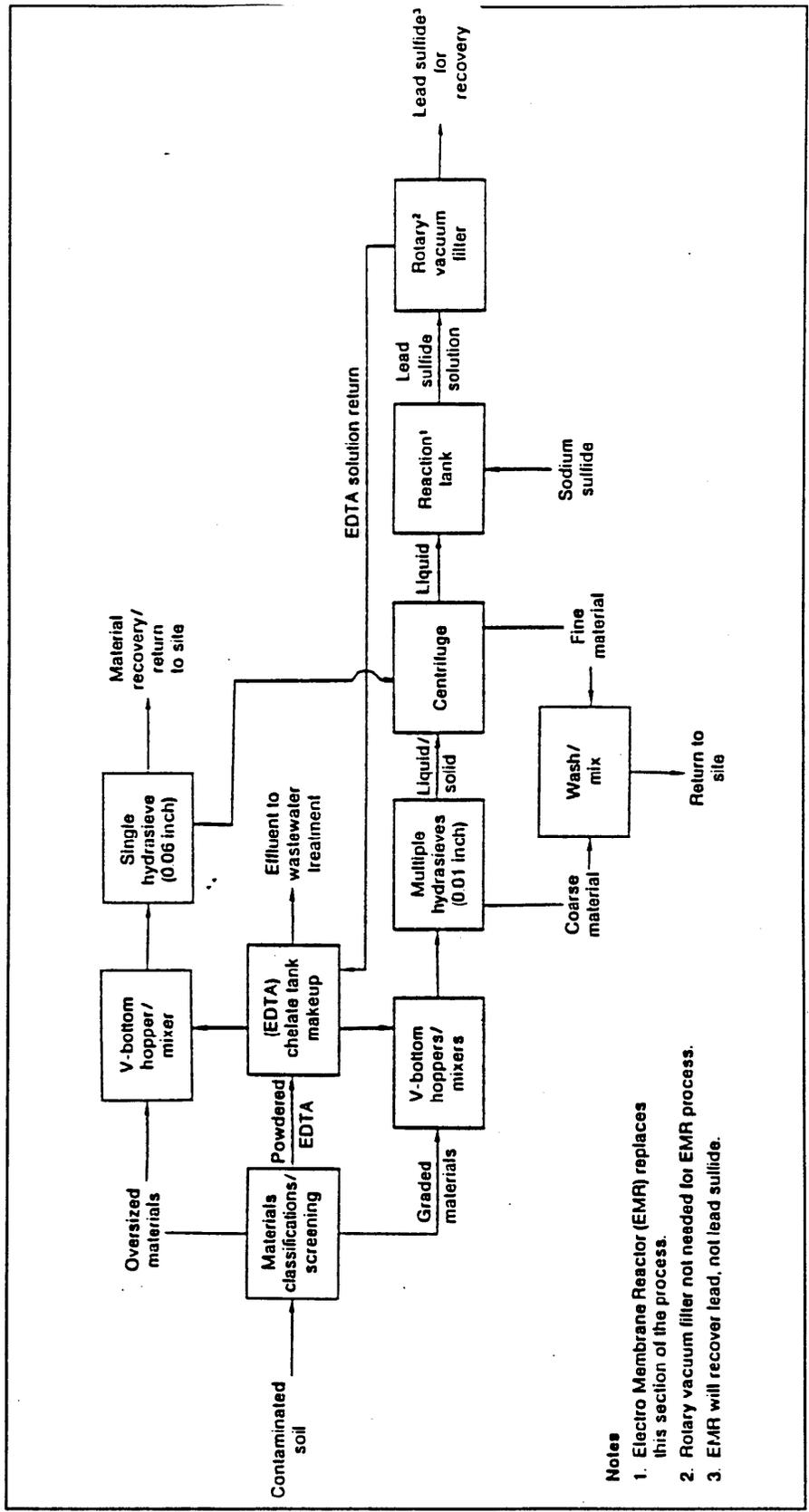


Figure 5. Schematic diagrams of soil treatment and leachate treatment for chromic acid-contaminated soil (after Yamamoto 1984)



- Notes**
1. Electro Membrane Reactor (EMR) replaces this section of the process.
 2. Rotary vacuum filter not needed for EMR process.
 3. EMR will recover lead, not lead sulfide.

Figure 6. Process flow diagram for continuous treatment of lead-contaminated soil (after Castle et al., undated)

would also impact the effectiveness of a given process. Chromic acid-contaminated soil was successfully treated below TCLP levels by water extraction alone. Laboratory studies indicate that lead can be removed below TCLP limits by EDTA and other treatment chemicals.

Long-term stability/performance. This process, when applied to heavy metal-contaminated soil, produces only decontaminated soil. Depending upon the level of cleanup, the treated soil can either be disposed at a nonhazardous landfill or backfilled at the site if compliance standards are achieved. No long-term problems are associated with the treated soil because the contaminants are permanently removed from the soil.

Residuals treatment/disposal requirements. The treated soil may require disposal at a landfill, depending on the residual metal concentrations in the soil. Of course, to be cost effective, the extraction must at least allow disposal in a less controlled and less expensive landfill. The spent extraction solution containing metals must also be treated prior to discharge. The metals may be recovered or concentrated for off-site disposal. Concentration by chemical precipitation most probably will result in hazardous sludges being produced, which in turn must be properly disposed. In addition, the soil extracts containing metals may significantly differ from typical plating or metal-finishing wastes. It is suspected that conventional precipitation or metals removal may not be easily adapted to contaminated soil. Extraction may be ineffective because of the complex mixture of materials in the extract. Thus, additional research may be needed to develop effective means of treating the metal-contaminated extracts.

Scale up potential. Treatment at the Navy site was conducted at a rate of 40 to 50 cu yd/day in a small-scale batch operation. Expansion of the hopper from 2 to 20 or 30 cu yd would increase capacity up to 15 times. Additional units in parallel could further increase capacity.

The continuous process could use existing ore or construction aggregate-processing equipment. While material handling of a mixed soil stream must be carefully designed, scale up should be readily achieved.

Potential disqualifiers. The principal concerns regarding the use of above-ground extraction are as follows:

- a. Mixtures of metals will probably require sequential extraction with multiple solutions, e.g., EDTA and acid.
- b. The spent extraction solution will require potentially difficult treatment.
- c. Disposal of metal solutions/sludges, as a hazardous material, will be required if reclamation is infeasible.

In situ extraction

Description. The basic theory behind this in situ process is the same as that for aboveground extraction. The only difference between the two processes is the manner in which the extraction chemicals are applied to the soil and then recovered. Usually, aboveground processes are preferred on sites where the contaminated soil has already been excavated as part of a removal action or where removal is mandated by other factors. Unlike aboveground processes, in situ extraction does not involve excavation of the soil. In situ processes involve application of the chemicals directly to the soil and subsequent recovery of the extracting agent from a treatment zone via the groundwater. While in situ extraction eliminates the cost of excavation and backfilling, this process carries a risk of contaminating the groundwater at a site, and may result in dilution of the elutriate and less efficient raw material utilization.

Extract solutions may be applied by spray application or flooding the contaminated site. The extraction fluid is subsequently recovered through subsurface drains or shallow well points, and is treated to recover the contaminants or concentrate them for disposal. Where expensive complexing agents are used, the treated extract solution may be recycled through the site to reduce costs. If the elutriate is not completely collected by either the subsurface drains or the shallow well point system, a potential risk of contaminating the ground or surface waters occurs (USEPA 1984b). Figure 7 presents a schematic diagram of this process.

An obvious advantage of this process over onsite extraction is that no costs are associated with excavation and handling of the soil. One disadvantage is the potential for short circuiting the low-permeability soils at sites with a heterogeneous soil profile.

Site-specific conditions, such as soil types, chemistry, and form of contaminants, will dictate the operating conditions, such as extraction chemical selection, solution concentration, and number of flushes and rinses.

Several methods for extracting metals from soils and sludges have been studied. These include shaker tests to evaluate the ability of the elutriating solution to remove the metals and subsequent soil column tests to determine metal removal from soils under continuous gravity flow. The types of elutriating solutions used in this process are the same as those used in aboveground extraction, namely acid/ NH_3 and EDTA/hydroxylamine/citrate/water.

While a few applications of the extraction process to onsite extraction of metals have been reported, pilot or full-scale in situ extraction installations for metals are unknown.

Treatment effectiveness. All the experimental data and limited field applications show that the process can be effective in removing metals. However,

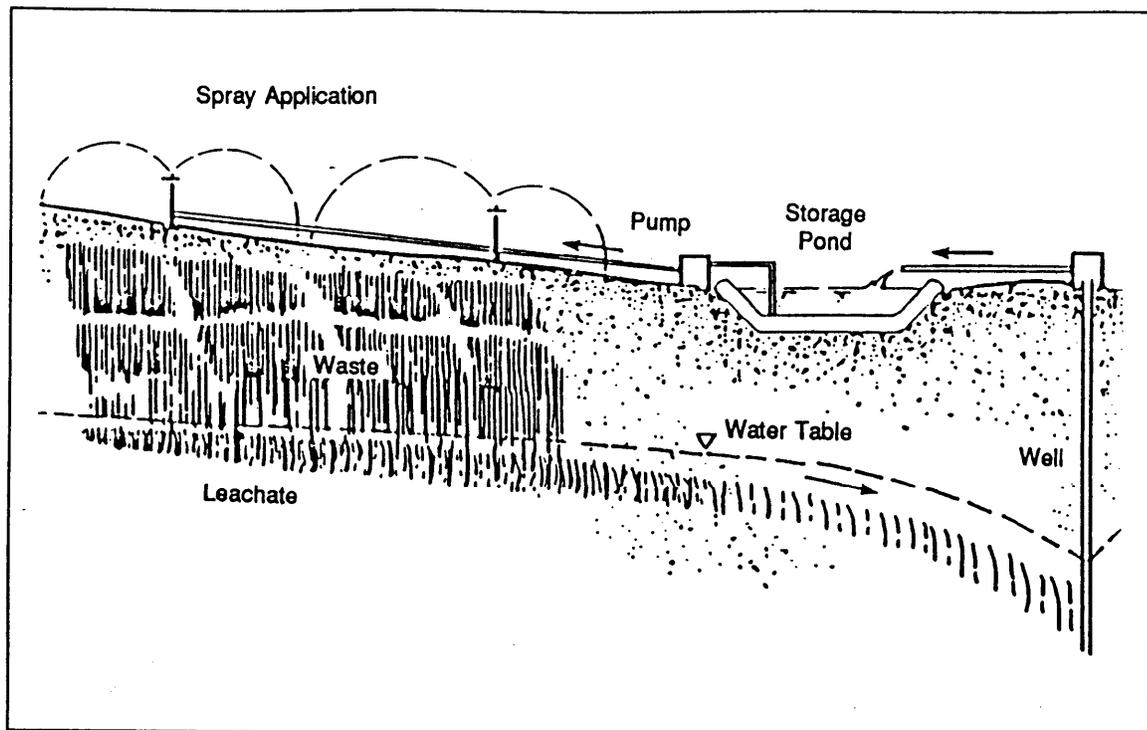


Figure 7. Schematic diagram of an in situ extraction process (from USEPA 1984b)

removal efficiencies depend on a number of site-specific conditions and the correct choice and sequence of solutions.

Ideally, the soil should be uniform and have moderate to high permeability. Sites with existing groundwater contamination are preferred since the treatment of such soils will not result in new contamination, and combined treatment of soil and groundwater is possible. Given appropriate site conditions, effective in situ treatment should be achievable.

Long-term stability/performance. Laboratory-scale performance data indicate that the process is effective, to varying degrees, in removing metals. From a concept standpoint this process has good long-term implications in that the source of contamination is removed from the soil. In situ treatment performance is typically monitored by discrete soil boring analysis. Therefore, heterogeneities, including low permeability zones that are not adequately treated, may initially go undetected.

Residuals treatment/disposal requirements. The greatest advantage of this process is that the soil is treated in situ and no disposal of the treated soil is necessary. However, the extraction fluid must be treated to remove the metals. Depending upon the economics, the metals would be recovered or would have to be disposed. In some instances, extraction fluids are used on a once-through basis and would have to be discharged following treatment.

Adaptability. Experimental data show that extraction methods can be used to remove metals from sludges and liquids. The data also show that the process can be used to treat soils contaminated with organics as well. However, treatment of soils contaminated with both may be difficult and would interfere with the ability to recycle expensive metal chelating agents. Sludge or incinerator residue treatment in situ is not likely to be advantageous because of the metal insolubility and relatively high concentrations.

Scale up potential. The process is very well suited to treating large soil areas. Treatment is expected to be completed sequentially from the surface to the depth of solution collection.

Potential disqualifiers. Principal concerns regarding the use of in situ extraction are as follows:

- a. The greatest risk in using this process is the potential for contaminating migration pathways such as ground and surface waters.
- b. Site conditions and present use may preclude or limit the use of this process at some locations.
- c. Certain metals and soils may not be amenable to efficient removal.

In Situ Adsorption

Description

Activated carbon or agricultural products could potentially be applied to soils to adsorb metals in situ. Adsorption of heavy metals by agricultural crop refuse and activated carbon was initially investigated for removal of heavy metals from wastewater. Activated carbon has been used extensively to treat wastewater for removal of organics. While this process has rarely been used exclusively for heavy metals removal, its performance in removing metals has been studied extensively.

Larsen and Schierup (1981) experimented with straw, sawdust, and activated carbon for the possible removal of heavy metals from wastewater. Their experiments have shown that 1 g of straw was able to adsorb from 4.3 to 15.2 mg of Zn, Cu, Pb, Ni, and Cd. They also showed that efficiency of removal by the straw was generally best with the addition of calcium carbonate (CaCO_3), a widely used metal precipitant. In a single treatment, the application of straw and CaCO_3 to 100 mg/L solution of metals could be used to remove the metals. However, removal efficiencies of Zn, Cu, Ni, and Cd remained below 50 percent. Lead removal was highest, at 85 percent. Sawdust was less effective for all metals. Activated carbon performance was higher (to 97.5 percent for Pb) but also generally unacceptable for removal of all metals. Column studies were conducted for continuous treatment of wastewater with barley straw. These showed that effective treatment

(>99 percent) could be achieved for these metals using a flow-through column system. Acid regeneration or thermal destruction of the straw could further concentrate the metals for recovery or disposal. The lower removals exhibited under single-stage batch conditions may be indicative of the behavior of straw incorporated into the soil for in situ treatment.

Henderson et al. (1977) investigated the adsorption of Hg, Cu, Ni, Cd, and Zn onto peanut hulls and raw and aged barks. These experiments were conducted to evaluate the feasibility of removing metals from wastewater using these natural waste products. The data showed that up to 80 percent removal of Cu was achieved in batch tests using smaller particle size peanut hulls, but removal of other metals remained below 60 percent.

Application of the above adsorption methods to the removal of metals from soils was a concept suggested as a potential treatment of metals-contaminated soil in a study conducted for the USEPA (1984). The technique would involve tilling the land to incorporate adsorbent materials such as agricultural waste products (see preceding paragraph) and activated carbon into the soil. Metals would be adsorbed onto these materials, thereby reducing mobility. The obvious advantage of using agricultural waste products is that they are inexpensive compared to activated carbon. It is common practice to use agricultural products and by-products as soil conditioners, e.g., manures and composts (USEPA 1984). Sewage sludge has also been used as a soil conditioner and a source of fertilizer. However, using sewage sludge as a means of adsorbing metals would prove to be counterproductive because the sludge itself may contain appreciable amounts of metals.

Treatment effectiveness

No specific studies are available on the application of ion exchange immobilization of heavy metals in soil. Studies on the treatment of wastewater indicate that a single-stage batch treatment (such as in situ soil treatment) may be inadequate to prevent migration of mobile metals. Other factors that could adversely affect adsorption capacity in soils include the presence of competing ions and chelating agents, low pH, and high ionic strength.

Theoretically, this method should be able to immobilize a portion of the metals in soil by adsorption. However, organic materials, such as agricultural crop refuse and activated carbon, are subject to microbial degradation, and this degradation may result in the subsequent release of immobilized metals (USEPA 1984). Finally, if the organic product or by-product has a high nitrogen content, microbial degradation may lead to elevated nitrate levels in groundwater.

Long-term stability/performance

While activated carbon is more stable than agricultural products, mineralization (microbial degradation) causes the release of sorbed metals, making this process effective only over the short term. Also, the dependence of adsorption on maintaining a near-neutral soil pH necessitates long-term monitoring and soil neutralization. To maintain initial performance, long-term, repeated applications of both the organic material and liming will be necessary.

Residuals treatment/disposal requirements

One advantage of this process is that no residuals must be disposed of since the treatment occurs in situ.

Adaptability

Few experiments have been performed to show that agricultural waste materials can be used to adsorb metals from wastewater. However, several studies have shown that agricultural products can immobilize organic chemicals, particularly pesticides, in soils (USEPA 1984). Likewise, activated carbon has been extensively used in wastewater treatment to remove organics, but is rarely used for removal of heavy metals alone.

Wastes containing both organics and metals may present a problem, since both of them are sorbable and organics are preferentially adsorbed by both activated carbon and agricultural products. This will cause metal adsorption to be decreased.

Scale up potential

The incorporation of adsorbents into near-surface soil can be readily accomplished using standard agricultural machinery.

Potential disqualifiers

Principal concerns regarding the use of in situ adsorption are as follows:

- a.* The ability of the process to immobilize metals in soil has not been demonstrated or tested. Extensive experimental and pilot-scale work remains to be done before applying the process on a full-scale level.
- b.* The performance of this technology applied to wastewater in batch studies indicates that only mediocre performance can be expected in application to soils.

- c. The long-term stability of the process is questionable. It would require extensive site management and possible repeated applications of the organic materials. In addition, site management in the form of diking would be necessary, as tilled soil is susceptible to erosion. Long-term monitoring would be necessary to ensure that no offsite migration of metals has occurred.
- d. Because of the above factors and because organics tend to alter soil properties such as water-holding capacity and bulk density, land use would be restricted.

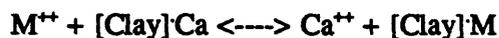
Ion Exchange Processes

In situ ion exchange

Description. The ion exchange process has been widely used to treat metal-contaminated wastewaters. The basic principle of this process is that metal ions that are in solution can be exchanged with ions that are bound to a suitable medium, usually a synthetic organic resin. Clay and zeolites also exhibit ion exchange properties and can be used in situ. While the applicability of ion exchange to treat metal-contaminated wastewaters has been demonstrated (Blount 1975, Gott 1978), its application to treatment of metal-contaminated soils is at the conceptual stage. This concept would involve incorporation of the zeolites and clays into the soil by tilling. Runoff and sedimentation control measures would be necessary because tilled sites are susceptible to erosion. The ability of these ion exchangers to remove metals is affected by factors such as those listed below (USEPA 1984c).

- a. pH.
- b. Competing cations.
- c. Presence of complexing agents.
- d. Soil solution ionic strength.
- e. Type of anions.

Clays have an affinity for metal cations and exchange calcium ions for them. This process has been characterized as follows:



Clays have been found to attenuate the migration of metals through soils, but little information is available on application of clay to soils for the purpose of immobilizing metals. Smeulders et al. (1983) studied the in situ immobilization of metals on clay by first complexing them with tetraethylenepentamine

(tetren). These investigators reported that the ion exchange behavior of heavy metals such as Cu, Zn, Ni, and Cd is strongly influenced by the tetren complex. They also indicated that clays have an increased affinity for the tetren-complexed heavy metals. Based on these results, a process that incorporates clay and tetren into the soil may result in more effective immobilization by ion exchange compared to using clay alone. Soils containing clay can be treated at a lower cost since commercial clay addition may not be necessary.

Synthetic ion exchange resins have been used for metals removal from low-strength industrial wastewater streams. The resin beads are stable polymerized hydrocarbons with various ionic functional groups on their surfaces that can exchange innocuous ions of calcium and chloride (Ca^{++} , Cl^-) for ions in solution. Application of ion exchange resin beads to the soil has been suggested for pesticides, but no experiments have been conducted. In situ application of resins has several potential disadvantages, including poor contact between beads and soil, high cost, and competition for exchange sites with naturally occurring ions.

Zeolites are natural hydrated aluminosilicate crystals with a typical chemical formula of $\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}$. They exhibit a selectivity pattern for certain metal ions (Cd, Cu, Pb, Zn) that is different from other ion exchange media and, in some ways, superior. Zeolites are relatively stable over a wide pH range (from 6 to 12) but degrade when the pH is below 4 or 5. They should be applied mainly to neutral or alkaline soils, or soil pH should be maintained by regular liming. High pH may have the added benefit of causing metals precipitation (USEPA 1984b).

While natural zeolites are used widely in industrial applications for water treatment (molecular sieves) and for agricultural applications (retention of ammonium and potassium), they have not been studied for in situ soil treatment. They do represent a less expensive alternative to ion exchange resins.

Treatment effectiveness. Natural zeolites and ion exchange resins have been found to be effective in removing heavy metals from water in full-scale applications. These processes are sensitive to pH and the presence of competing ions. No data are available for direct application to soils.

The research on enhancing the immobilization of metals on clays by the addition of a complexing agent (tetren) appears promising. Experiments reduced the soluble metal levels as much as two orders of magnitude as compared with clay alone. Higher metal ion concentrations in particular exhibit improved performance. For example, the concentration of copper in solution was reduced below 1 ppm, while producing a clay-tetren loading of 1,000 ppm copper (Smeulders et al. 1983). The process may be less effective for lower concentrations of metals and where high levels of cations (Na^+ , Ca^{++} , Fe^{++}) may interfere with the capture of heavy metals (USEPA 1984b).

Long-term stability/performance. No studies have been conducted to determine the long-term stability of this process and its ability to immobilize

metals in soil. If zeolites are used, long-term site management (including liming and maintenance of erosion controls) would be necessary. Similar potential impacts may be expected for resins or tetren-clay mixtures.

Residuals treatment/disposal requirements. This is an in situ process, and no residuals must be disposed since the immobilized metals stay within the soil.

Adaptability. The clay-tetren process and ion exchange resin process may be also be used to treat sites contaminated with certain organics along with metals if the organics are sorbed by clay. Zeolites, on the other hand, are only for treatment of heavy metals. The ability of the resin and zeolite processes to treat metal-contaminated liquid wastes at low concentrations is well established, but successful treatment of high concentration sludges is unlikely. Treatment of residues from organic treatment processes may be feasible, but onsite processing may be more appropriate than in situ processing.

Scale up potential. The in situ process would use common agricultural machinery capable of treating large soil surface areas at limited depths.

Potential disqualifiers. Principal concerns regarding the use of the in situ ion exchange process are as follows:

- a. The process, as applied to soils, is still in a conceptual stage. Therefore, little information is available on treatment effectiveness, process parameters, cost, etc., with the exception of the clay-tetren process.
- b. The long-term stability of the process is questionable, as ion-exchange media are typically sensitive to pH.
- c. The process may be less effective in sites where heavy metals are present in trace amounts and when excessive amounts of ions such as Na^+ , Ca^{++} , and Fe^{++} are present in the soil.

Aboveground ion exchange

Description. Ion exchange was proposed by Sen Gupta (1986) as a technique for metal removal from waste ash or sludges that contain low concentrations of metals. The waste would be slurred in water and mixed with ion exchange resin beads. Although metal solubilities in water may be low, the selection of a resin with a high affinity and selectivity for the metal would result in removal of the metal compounds from solution and a continued driving force for solubilizing metals from the waste. Preliminary laboratory studies showed that most lead carbonate was removed from a slurry within 2 hr.

Following completion of slurry transfer, the slurred waste is drained while the resin beads are retained by a basket strainer for subsequent regeneration.

The slurry can be dewatered and disposed as a nonhazardous waste. A process schematic is shown as Figure 8.

The application of this technology to contaminated soils would necessitate a modification of materials handling to include prescreening soil particles or devising an alternative slurry/resin separation technique (e.g., flotation).

Treatment effectiveness. Ion exchange resins have been used successfully to remove metals from wastewater to extremely low levels. If adequate dissolution of metal compounds can be sustained throughout treatment, low concentrations can be achieved in the treated soil. Since the effectiveness depends on concentration, metal species, resin characteristics, conjugate ion or molecule concentrations, and competing ions, its effectiveness must be tested for each soil/metal matrix.

Another consideration in assessing the effectiveness of the technology is the form of the metal-containing residual stream. If resin loading is inadequate for the particular soil/metal input, the volume of metal concentrate solution may be too high relative to alternative techniques (e.g., extraction with acids or chelating agents).

Long-term stability/performance. Since metals are removed from the soil, no long-term performance concerns exist.

Residuals treatment/disposal requirements. The concentrated regeneration solution and lower concentration rinse solutions require further treatment or disposal. These solutions can be treated by conventional chemical precipitation techniques (e.g., lime, sulfide) or with alternative recovery techniques (e.g., electrodeposition). The more cost-effective precipitation process will result in a concentrated sludge for further treatment or probable disposal as a hazardous waste.

Adaptability. Significant destruction or capture of organics is not expected. Treatment of soils contaminated with organics may prove difficult if significant solubilization occurs in the slurry filtrate or if ion exchange fouling results. Residues from organic treatment processes may be treated. High-concentration sludges (or soils) would not be efficiently treated because of the limited capacity of ion exchange resins.

Scale up potential. The process includes numerous processing and separation steps but should be readily scaled up with available processing equipment.

Potential disqualifiers. Principal concerns regarding the use of the above-ground ion exchange process are as follows:

- a. As metal concentrations and competitive ion concentrations increase, the volume of regenerant increases. Under these circumstances, the

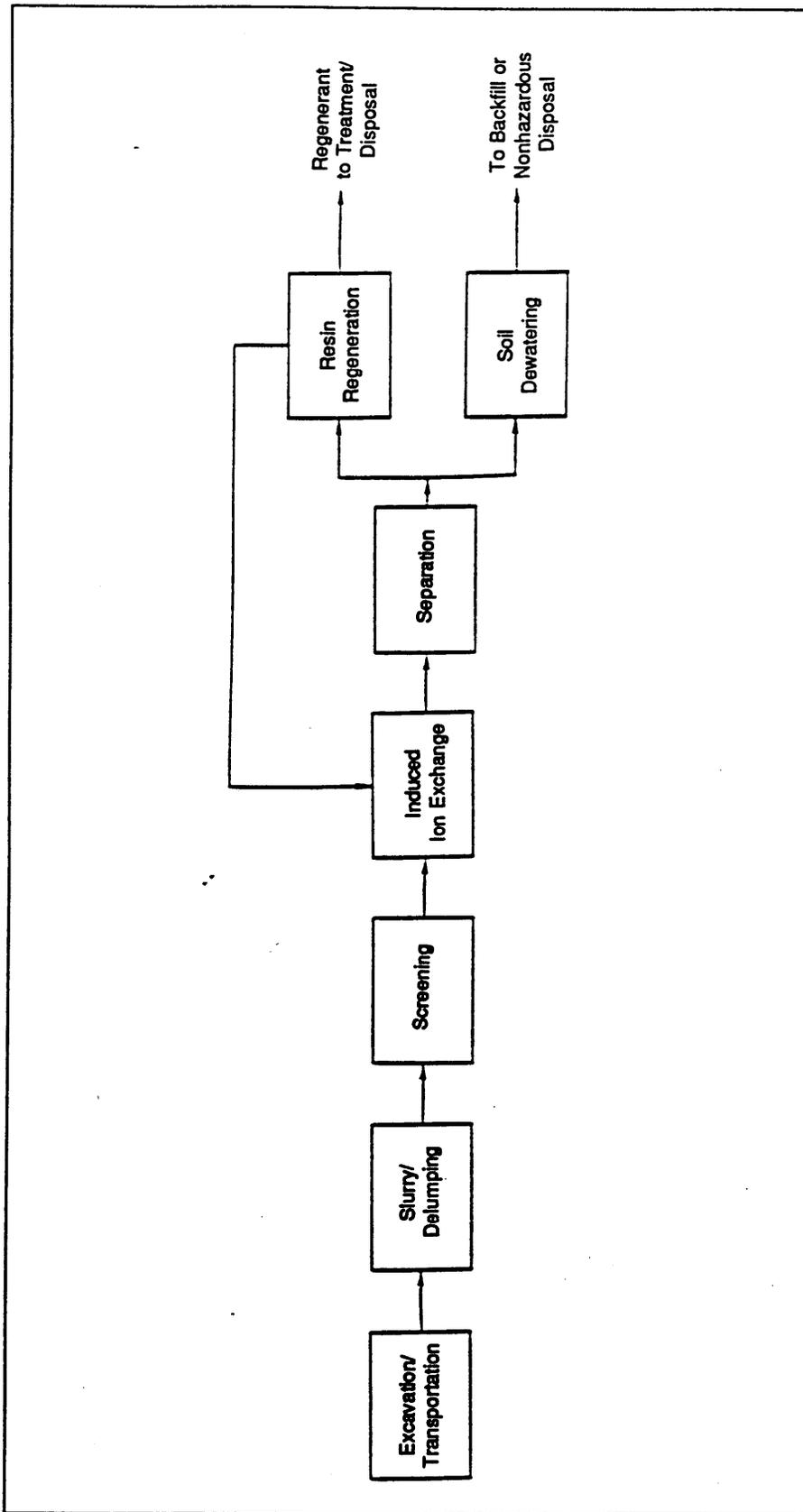


Figure 8. Schematic of aboveground ion exchange process (from Weston 1987)

objective of this treatment (to create a low-volume concentrated metal-bearing stream while treating soil) might not be met.

b. Further processing and residuals disposal will be necessary.

High-Gradient Magnetic Separation

Description

High-gradient magnetic separation (HGMS) has been studied for removal of magnetic or paramagnetic substances from wastewater and certain mineral products, including clays and coal. A filamentous ferromagnetic material immersed in a magnetic field provides a high surface area for capture. Stainless steel wool or expanded metal packing have been used.

Some nonmagnetic materials can be removed by "seeding" with a ferromagnetic substance such as iron sulfate (Fe_2SO_4) to create an agglomerate. This coprecipitation process has been used successfully for metals removal from wastewater by flocculation/clarification. Here, nonmagnetic metals are bound to a magnetic agglomerate prior to magnetic separation.

The material must be first processed for size reduction and is then conveyed using a water slurry or air. The material passes through the magnetic matrix under a magnetic field of 1,000 to 20,000 gauss. The steel wool is magnetized, creating high-magnetic field gradients locally around each fiber. This can result in capture of even weakly paramagnetic particles. The magnetic field is periodically removed to release the accumulated metals into a slurry or air concentrate. A process schematic is presented as Figure 9.

HGMS was first commercialized in 1974 for removal of mineral impurities from clay slurries. It may also be applied for recovery of metals from process effluents and low-grade ores and removal of iron from river water. It has also been used successfully on a commercial scale for coal desulfurization and demineralization at a rate of 100 tons of dry coal per hour. Capital outlay varies with the strength of the magnetic field. Operating costs are estimated at \$1 to \$5 per 1,000 gal for removal of paramagnetic materials from liquids (Kiang and Metry 1982).

While HGMS has been applied to finely ground dried coal (30 to 100 mesh) using air conveyance, testing is currently being conducted in a joint Department of Energy/Department of Defense/USEPA project for separating metals from waste sludges, slurries, or granular mixtures. This study will also determine if diamagnetic materials (those repulsed by a magnet) can be separated by using an open-gradient magnetic separator (OGMS). The OGMS process provides a high-gradient magnetic field across a gravity-fed flow of material without a magnetized matrix. The paramagnetic or diamagnetic materials are deflected from the vertical and can be captured in separate receiving vessels. This process offers continuous operation and reduced material

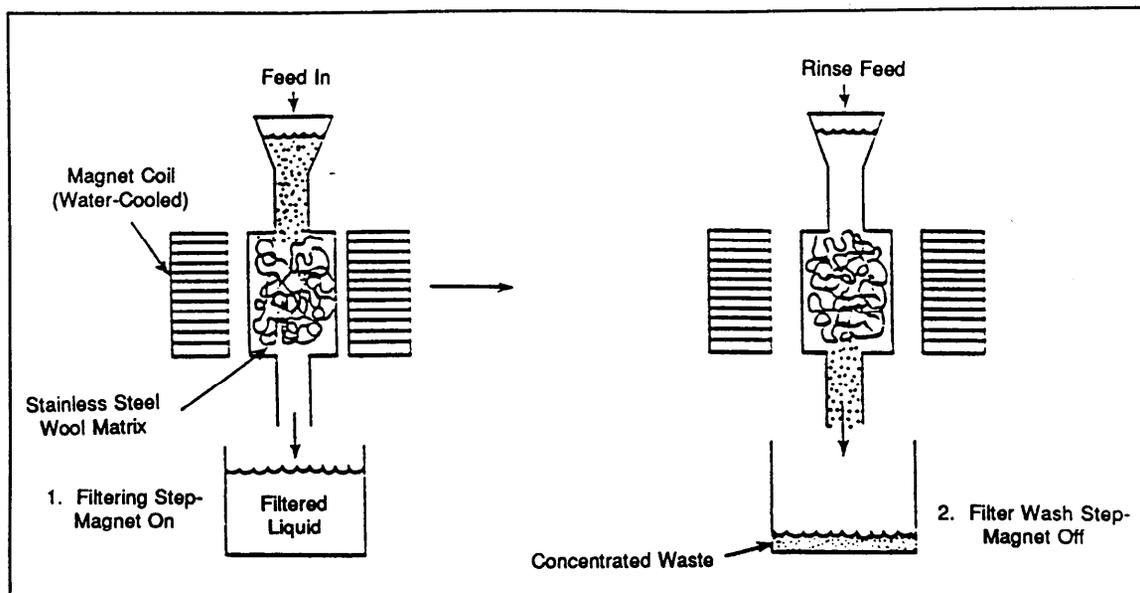


Figure 9. Schematic representation of HGMS for liquid streams (from Bove et al. 1983)

handling problems. This process has been laboratory tested on a bench-scale Franz open-gradient magnetic separator. A small super-cooled laboratory pilot unit will be tested as well.

While no test results have been published on OGMS, preliminary results are available for separation of uranium from sand or sandy soils. Thus far, recovery of a uranium-rich stream (30 to 50 percent) has been confirmed, but the treated stream still retained 0.2 to 0.4 percent uranium.

The applicability of HGMS and OGMS appears to be limited to solid materials that can be separated into contaminated and uncontaminated particles when dried, and reduced in size to 30 to 100 mesh. Its best applications appear to be in metallurgical or mineral processes where impurity removal in the fraction of a percent range is adequate. Further testing will be necessary to determine if lower treatment levels are achievable.

One limitation with regard to application of HGMS and OGMS to soil or wastes is the magnetic susceptibility of the target compounds. Metals and their various molecular species exhibit wide variations in magnetic susceptibility. Some metals have magnetic values very close to major soil components (e.g., silica). As a result, mixed metals and metal species may not be as easily treated as single-specie contamination.

Treatment effectiveness

The HGMS process is effective for removal of impurities (ferrous material, pyritic sulfur, ash) from clays and coal where objectives range from fractions

of a percent to 40-percent impurities. Removal of metal contaminants in soils to the low-parts per million range has not been demonstrated experimentally. The process may have limited application for highly contaminated soils with appropriate paramagnetic properties where the metals are separable as particles rather than dispersed. While complete decontamination may not be achieved, HGMS/OGMS can be considered for large applications as a pretreatment/recovery step.

Long-term stability/performance

The process would remove metals from the soil. Therefore, if adequate treatment can initially be achieved, the removal of the hazardous properties will be permanent.

Residuals treatment

The HGMS and OGMS processes produce a concentrated liquid or solid waste that will require further treatment and/or disposal as a hazardous waste. To achieve a lower concentration in the treated stream, the volume of the concentrate would likely increase.

Adaptability

HGMS cannot directly treat for organic compounds. However, a pretreatment to associate the organic contaminants with a magnetic fraction can, in some cases, overcome this limitation. The HGMS process might be useful for treating sludges, but it is not likely to further significantly concentrate already concentrated sludges. The treatment of incineration residues may be possible only if metals are not dispersed in the slag. The OGMS process is not likely to be useful for mixed property soils such as sandy clays, because drying and particle size reduction will result in too wide a variation in particle size, making separation difficult.

Scale up potential

HGMS has been demonstrated for large commercial applications (i.e., coal, clay processing). OGMS is a continuous process that does not require back-flush cycling (as does HGMS), so scale up should also be readily achievable.

Potential disqualifiers

The principal concerns regarding application of HGMS/OGMS are performance and residue management. No other significant fatal flaws have been identified.

Electrochemical Separation

Description

Electrochemical processing of soils has been investigated and used over the last 50 years since its first application (Casagrande 1957) for improving the stability of excavations; increasing pile strength; stabilizing fine-grained soils; dewatering foams, sludges, and dredgings; groundwater lowering and barrier systems; removal of salts from agricultural soils; and separation and filtration of materials in soils and solutions (Mitchell 1976). Electrokinetic soil processing using low-level direct currents (in the order of magnitude of milliamps/cm² of electrode area) could potentially be used as an in situ separation/removal technique for extracting heavy metals and radionuclides from soils (Acar et al. 1989).

Electrochemical processing of contaminated soils separates the ionic species from the soil by passing a low direct current (DC) through it. Coupling between electrical, chemical, and hydraulic gradients is responsible for different types of electrokinetic phenomena in soils. These phenomena include electroosmosis, electrophoresis, streaming potential, and sedimentation potential (Casagrande 1957). Electroosmosis and electrophoresis are terms applied to the movement of water and particles, due to the application of the low-DC current. Streaming potential and sedimentation potential, conversely, are the generation of a current due to the movement of water and particles, respectively.

The effect of this coupling becomes more important in fine-grained soils with lower coefficients of permeability (Mitchell 1976). For instance, the electroosmotic flow rate (q_e) is defined as

$$q_e = (k_e)(i_e)(A)$$

where

k_e = coefficient of electroosmotic permeability

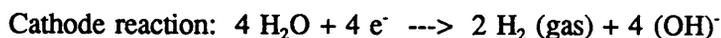
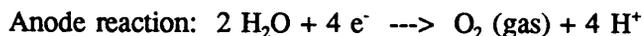
i_e = electrical potential gradient

A = cross-sectional area

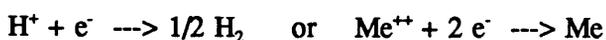
Estimates of electroosmotic (EO) flow rates can be made using this equation. The value of k_e varies within one order of magnitude for all soils, 1×10^{-5} to 1×10^{-6} (cm/sec)/(v/cm), with the higher values being at higher water contents. When compared with the five- to six-order of magnitude decrease in hydraulic conductivity from fine sands to clays (1×10^{-2} cm/sec to 1×10^{-8} cm/sec), it is evident that flow rates comparable to those achieved by very high hydraulic gradients in low-permeability soils could be obtained with very low electrical gradients (Casagrande 1957).

Figure 10 illustrates the electrical gradients, the hydraulic potentials, and the ion flow during the process under constant current conditions. The ion flow and electrochemistry associated with electrokinetic soil processing are still not well understood, but the need for new and more efficient metal removal methods has prompted some recent work on the methodology (Acar et al. 1989).

The predominant electrode reactions in a typical low-ionic strength soil solution with inert electrodes would be



Other secondary reactions would be expected to occur depending upon the concentration of the reactants, for example:



The production of H^+ ions at the anode decreases the pH while the reaction at the cathode increases it. The pH values of 2 at the anode and 13 at the cathode are those typically found (Casagrande 1957). For the same quantity of electricity, twice the amount of water is hydrolyzed at the cathode than at the anode. Thus, not only is a hydraulic gradient produced, but because of a buildup of H^+ at the anode, a chemical gradient is also induced. In addition, other ionic species can be produced if electrolyzable electrodes (aluminum, steel, silver, etc.) are used.

As a result of the pH gradients set up by the electrode reactions, the following physicochemical interactions would be expected:

- a. Dissolution of the clay minerals beyond a pH range of around 7 to 9.
- b. Adsorption/desorption and exchange of cations by replacement of H^+ and OH^- .
- c. Precipitation of salts and metal ions in very high or very low pH environments can produce cementitious products.
- d. Changes in the structure and, hence, the engineering characteristics of the soil due to variations in the pore fluid chemistry.

All of these interactions have been reported (Casagrande 1957). The movement of the pH front by migration and advection leading to the desorption and solution of inorganic cations from the clay surfaces together with the concurrent electroosmotic flow process constitutes the fundamental mechanism by which inorganic cations could be removed from fine-grained soils.

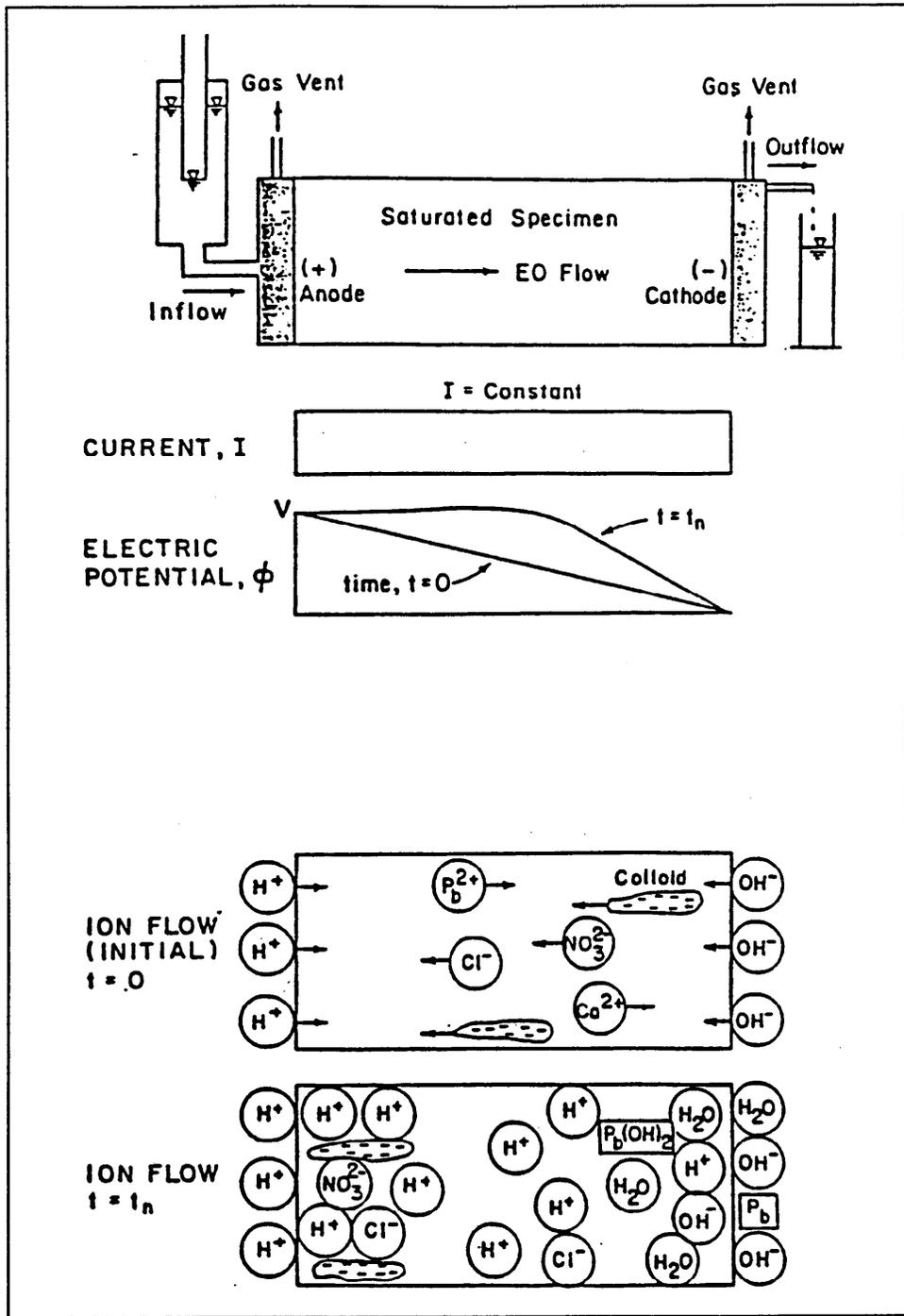


Figure 10. Schematic diagram of electrokinetic soil processing and ion flow (after Acar et al. 1989)

Treatment effectiveness

Hornog and Banerjee (1987) investigated the use of electrokinetics for the remediation of the United Chrome Superfund site near Corvallis, OR. The area selected was approximately 0.6 ha of level ground. This areal extent, a nearly static groundwater regime, and the saturated, moderately permeable soils at a shallow depth were found to be favorable for maximizing the effectiveness of electrokinetics. Hexavalent chromium (Cr VI), which was the most prevalent of the contaminants, existed primarily in the anionic forms CrO_2^- , HCrO_4^- , or $\text{Cr}_2\text{O}_7^{2-}$, depending on the concentration of the individual chromium ions and the pH of the soil. Because chromates, which do not react with soil particles, were the major ionic species, transport of the ions through the soil matrix at this site was achieved with high efficiency and with relatively low power consumption (Renaould and Probststein 1987). These investigators concluded that a treatment combination of hydraulic leaching and electrokinetics would accelerate chromium removal compared to hydraulic leaching alone. They also surmised that the possible methods of action involved were dispersion due to hydraulic flow, ion migration, water electrolysis, adsorption/desorption, and chromium reduction due to the applied electric field.

Additional research and field trials must be undertaken to ascertain the effects of different electrodes composition, soil types, and pore fluid compositions on the efficacy of the process.

Long-term stability/performance

The removal of the metal ions from the soil would produce a permanent solution. A concentrated by-product containing the removed ions would have to be treated and disposed.

Residuals treatment/disposal requirements

No residuals remain in the treated soil. However, the concentrated metal solution removed from the site would have to be treated and disposed, or reclaimed.

Adaptability

The process seems to be best suited for fine-grained soils with low levels of organic matter and low metal concentrations. Metal ions that have low levels of interaction with the soil matrix appear to be better candidates for the process. There is some question as to how large an area could be treated with a single application, but clean-up activities associated with the Soviet nuclear disaster (Chernobyl) indicate the potential large-scale application of this technology.

Scale up potential

No information is currently available concerning the rate of cleanup. Electrokinetics would probably be used to enhance metal removal by hydraulic leaching from soils with low permeability.

Potential disqualifiers

The principal concerns regarding the application of electrochemical separation are listed below.

- a. Inhomogeneity in typical soils may cause uneven voltage gradients.
- b. Feasibility may depend on local power costs.
- c. Metal removal rates may not be high enough to be effective.
- d. Organics or high ion concentrations may interfere with the beneficial electrokinetic action.
- e. Insoluble metal species will not be affected.

Physical Separation

Description

Heavy metals contamination can exist in soil in several forms. Lead paint deterioration, sand blasting, and firing range operations produce discrete fragments or metallic smears on soil particles. Electroplating, battery reworking, and cooling tower discharging can produce ionic metals associated with soil particles.

Each "type" of metals contamination exhibits different "physical" properties: particle size, density, and surface charge depending upon the metallic particle or the associated soil particle. As a result, the contamination will occur, not uniformly in the soil, but distributed according to these physical properties. For instance, most adsorbed metals are associated with smaller soil particles.

Recent research exploits the distribution of metals in soil/sediment by physically removing smaller, contaminant-rich particles. Ideally, the "cleaned" fraction will require no further treatment, and the "concentrated" fraction can be more economically processed. An important example of this approach is the remediation of low-level radioactively contaminated soil. The major parameters affecting the association of a heavy metal with soil and sediment include grain size, surface area, geochemical substrate, and metal affinity, as illustrated in Figure 11.

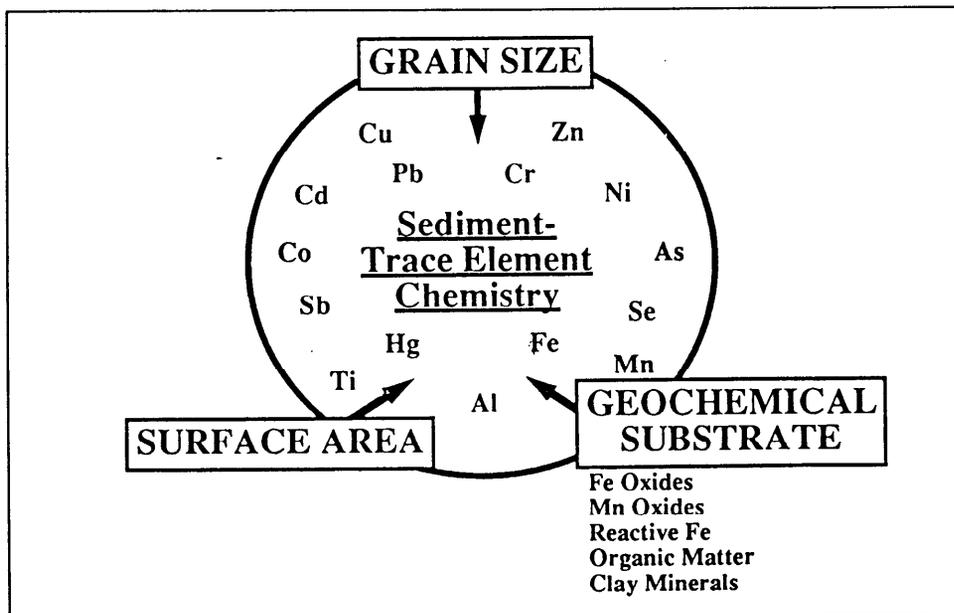


Figure 11. Geochemical factors affecting sediment-trace element chemistry (after Horowitz 1991)

Heavy metals predominantly associate with smaller, higher surface area particles. They preferentially adsorb (or coprecipitate) with hydrous manganese and iron oxides, organics, and clay minerals.

The general approach in physical separations remediation is to use processes commonly applied in the minerals processing industry. These processes exploit differences in particle size, density, surface, and other properties to effect a separation. A typical process chain might begin with a scrubbing trommel. The soil flows into a rotating drum fitted with interior baffles and water spray. The rolling motion and the water condition, scrub, and declump the soil. The soil then moves to the outlet where smaller material falls through a cylindrical screen mounted around the mouth of the drum. The oversized material rides to the edge of the screen and falls into a chute.

First-stage products (oversized and tailings) go on to secondary separation. Tailings might go to a "cleaning" or "concentrating" stage to concentrate contaminants into an even smaller volume. This approach can be taken, if the contamination is preferentially associated with a distinct soil density fraction. A spiral concentrator is frequently used for this stage. As a soil/water slurry spirals down, the heavier soil fractions accumulate toward the inner radius and the less dense fraction moves toward the outer radius. The concentrate stream passes through the take-out ports.

By the end of this stage, the soil has passed through separations based first on size and then on density. Further separations based on density difference may employ centrifuges or shaking tables. Differences in surface effects may be exploited with a flotation cell.

Several groups have applied processes similar to those described here to physically separate the more contaminated fractions of soil. Companies and government agencies include the following: AWC, a Lockheed company; USEPA laboratories at Montgomery, AL, and Edison, NJ; and the Bureau of Mines.

The USEPA laboratory at Montgomery (National Air and Radiation Environmental Laboratory, NAREL) has remediated soil contaminated with low-level radioactivity. Most of the radiation originates from fine particles of monazite. The treatment strategy involves vigorous agitation of a soil-water slurry in a trommel to liberate the fine particles. This is followed by screening at the trommel outlet to remove gravel-size material. The finer tailings then go to hydrocyclones to remove the -70 mesh fines containing most of the radioactive material. Figure 12 shows the trailer-mounted main separations unit with the trommel and hydrocyclones. It should be noted that two trailers of equipment are provided for effluent water treatment--a settling tank and filter press.

"Phase I" trial runs have been made using low-level radioactively contaminated soil from an ore processing plant in Wayne, NJ (the "Wayne Interim Storage Site"). They have run the system at steady state separating the -70 mesh material and getting 30 percent recovery of soil meeting



Figure 12. USEPA-NAREL trailer-mounted physical separations unit (system for low-level radioactively contaminated soil)

radioactivity limits. Adding equipment to give a -200 mesh cut should give 50 percent recovery.¹

In another effort, the Naval Civil Engineering Laboratory has worked with the Bureau of Mines at Salt Lake City to remediate small arms firing range soil. The investigators have characterized significant aspects of lead contamination at a firing range, including dispersal of lead over the area, transport into surface water, and uptake by plants. Based on this information, the Bureau of Mines has carried out a protocol to select methods and processes to provide an integrated process concept for lead removal.

Figure 13 shows the conceptual process flow sheet. Mineral processing unit operations have been operated on a small pilot scale to produce soil fractions. These include bullets and fragments, a coarse gravel material, fines

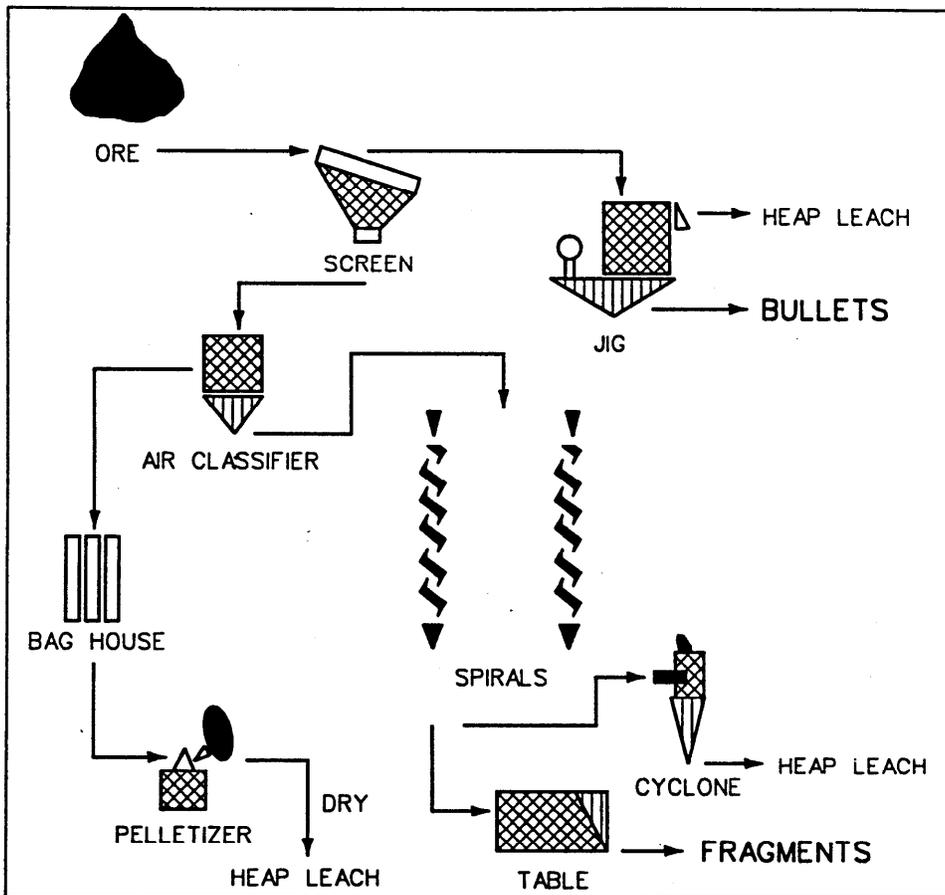


Figure 13. Proposed flowsheet for physical separation of lead from firing range soil (from U.S. Bureau of Mines 1991)

¹ Personal Communication, 1991 (Dec), Clint Cox, Project Engineer, USEPA-NAREL, Office of Radiation Programs, Montgomery, AL.

with 2 percent fine (slimes) lead particles, and wood fragments with embedded lead particles.

All fractions failed the TCLP test for lead. However, about 95 percent of the total mass of lead was removed, and the resulting fractions were sorted for more efficient leaching. Bench-scale acid extraction produced products that met the TCLP limits.

Treatment effectiveness

Remediation of radioactively contaminated soil has shown that 30 to 50 percent of the soil can be very readily cleaned to meet standards for back-filling. With secondary physical and chemical cleaning, up to 90 percent of the soil may meet standards. Physical separation of firing range soil removed 95 percent of the mass of lead. Resulting soil fractions failed the TCLP for lead but passed after supplementary heap leaching.

Overall, physical separation can achieve a number of benefits that translate to reduced treatment costs. These benefits include concentration of the contaminant in a smaller volume, removal of the bulk of the contaminant, and separation of the soil into size fractions for more efficient secondary treatment. In some cases, physical separation may achieve the majority of the cleanup. Most onsite remediation approaches could benefit to some extent from physical separation.

Long-term stability/performance

The bulk of the contamination will be removed from the site and concentrated in a fraction of the original soil. The "cleaned" soil will contain only minor traces of metal contamination. Soil left at the site must meet stringent standards based on content and/or leach testing. Accordingly, this approach should present no long-term stability/performance concerns.

Residuals treatment/disposal requirements

The bulk of the contaminants will reside in a fraction of the original soil volume. Slurry water will also contain some contamination. The contaminant-enriched soil may require disposal at a secure landfill or additional treatment, e.g. chemical extraction, to allow less restricted disposal. Slurry water will require flocculation of suspended particles (typically enriched in contaminants). The water may have to be treated.

Adaptability

Both organics and metals tend to concentrate in the smaller particle size fractions. Physical separation may thus enrich both contaminant types into a fraction of the original soil volume, allowing treatment of such combined wastes. In addition, physical separation has been adapted to a number of media: radioactively contaminated soil, soil with bullet fragments, and polychlorinated biphenyl (PCB)-contaminated sediment. Promising results indicate that physical separation is not only adaptable, but a necessary step prior to many treatments such as bioremediation, incineration, and low-temperature devolatilization. In some cases, large fractions of "clean" soil may be recovered. In other cases, the physical separation may simply improve efficiency by removing the bulk of the contaminant or producing a more uniform feed for secondary treatment.

Scale up potential

Demonstrations have been performed for remediation of radioactively contaminated soil up to rates of 15 cu yd/hr. Pilot-scale work indicates no problems with scale up of methods for remediating firing range soil. In general, all the major unit operations required are well developed for use in the mining industry. Fortuitously, many systems for placer mining are built for small-scale, mobile operations.

The research and development (R&D) needs focus on soil/contaminant characterization and determination of separations performance for process design. Finally, R&D needs exist in novel approaches, for example, to treat combined metal and organic wastes or to apply ultrasound for particle cleaning.

Potential disqualifiers

Principal concerns regarding the application of physical separation technology are as follows:

- a. Small pockets of unusual contaminant combinations may not warrant the characterization and testing required to configure a separations system.
- b. Benefits will be limited where contamination occurs uniformly throughout the soil or separation does not remove any significant fraction of the contaminant. Given the fundamentals of soil/metals association and results to date, such cases are probably uncommon.

3 Thermal Processes

High-Temperature Fluid Wall Reactor

Description

The high-temperature fluid wall (HTFW) reactor was developed by J. M. Huber Corporation of Borger, TX, and patented in 1983. This process uses radiative heat to pyrolyze the waste components to elements or simple compounds. At the heart of the HTFW reactor is a cylindrical porous graphite "core" through which waste material flows. The annular space between the inner cylinder and another outer cylinder contains the carbon electrodes. These electrodes, operated at temperatures of 4,200 to 4,300 °F, are heated electrically. The electrodes, in turn, heat the graphite core to incandescence at a temperature of 4,100 °F.

Waste materials are gravity fed into the core from the top of the reactor. A constant flow of nitrogen through the annulus and porous core results in a fluid barrier being formed between the waste materials and the core (hence, the name "fluid wall" reactor). Various other inert gases, such as argon, can be used to act as a fluid wall. Elimination of contact between the waste materials and the core reduces maintenance problems such as fouling. Solids must be reduced in size to 10 mesh or smaller and dried prior to processing.

Unlike combustion processes, the waste materials are heated by radiation rather than convection or conduction and can be processed in the absence of oxygen. The company estimates that the radiant power density is approximately 1,200 W/sq in. The waste materials are rapidly heated at a rate of 10^5 to 10^7 °F/sec (Lee, Schofield, and Lewis 1984). Organic wastes are pyrolyzed at these temperatures, resulting in their conversion into basic elements or simple molecules that reside in the gaseous phase. Inorganic wastes or residues (which may include nonvolatile heavy metals) are vitrified along with clay and other minerals in the soil to form glassy, granular materials. This vitrified material has a very low potential for leaching contaminants and thus may be disposed in a nonhazardous landfill.

In the additional reacting chambers that follow the HTFW reactor, the gaseous phase is maintained at high temperature for further reaction and then

cooled. After cooling, the granular vitrified solids drop into a sealed container for disposal or backfilling. Subsequently, the gases are sent through a baghouse for particulate removal, followed by a scrubber for chlorine removal, and finally through an activated carbon column that acts as a backup chlorine and organics removal device. Scrubbing and activated carbon gas treatment steps are necessary for chlorinated hydrocarbon processing only. Figures 14 and 15 show sections of a HTFW reactor.

Huber Corporation presently has a stationary pilot unit with a 12-in. core diameter and a transportable unit with a 3-in. core diameter. The maximum feasible throughput size of a transportable unit was estimated to be 20,000 to 30,000 tons/year. Huber Corporation has estimated that for a large site (100,000 tons of material), the cost per ton would be in the range of \$365 to \$565. The breakdown of the costs is as follows: labor, 7 percent; maintenance, 12 percent; depreciation, 18 percent; energy, 29 percent; and other (including permitting), 34 percent.

Treatment effectiveness

The available literature shows that the process has been successfully used in the destruction of PCBs and dioxins in contaminated soil. These tests were performed at the experimental and pilot levels. Because of the high temperature in the reactor, very high destruction efficiencies are achieved since destruction is by pyrolysis. Since the reactor operates in an inert atmosphere, no oxygen-containing by-products such as dioxin are formed. In 1986 the Huber Corporation also studied the fate of metals under a contract from the U.S. Air Force. The company did not specifically design the process to remove or treat for metals, but examined the fate of metals while evaluating the ability of the process to destroy organics. Metals, especially those such as mercury and arsenic with lower boiling points, vaporize, and may recondense on particulates. The investigators in this reported study concluded that the remaining heavy metals end up in the vitrified phase, which is thought to have a low leachability. Test data show a reduction in leachability of some metals, but no data are available to confirm this for incinerator feeds containing high metals concentrations. Related information from incineration studies indicates that metals can escape to and beyond the baghouse. This escape may not be limited to the more volatile metals. As much as 30 to 40 percent of the metals may pass through the baghouse, creating an air pollution problem (Greenberg et al. 1978, Carlsson 1986).

Long-term stability/performance

The process results in the effective treatment of organic wastes and volatilization/condensation of certain metals from contaminated soil. The remaining inorganic waste materials end up in a granular glassy form. This glassy material is thought to be nonhazardous and very stable. Once formed

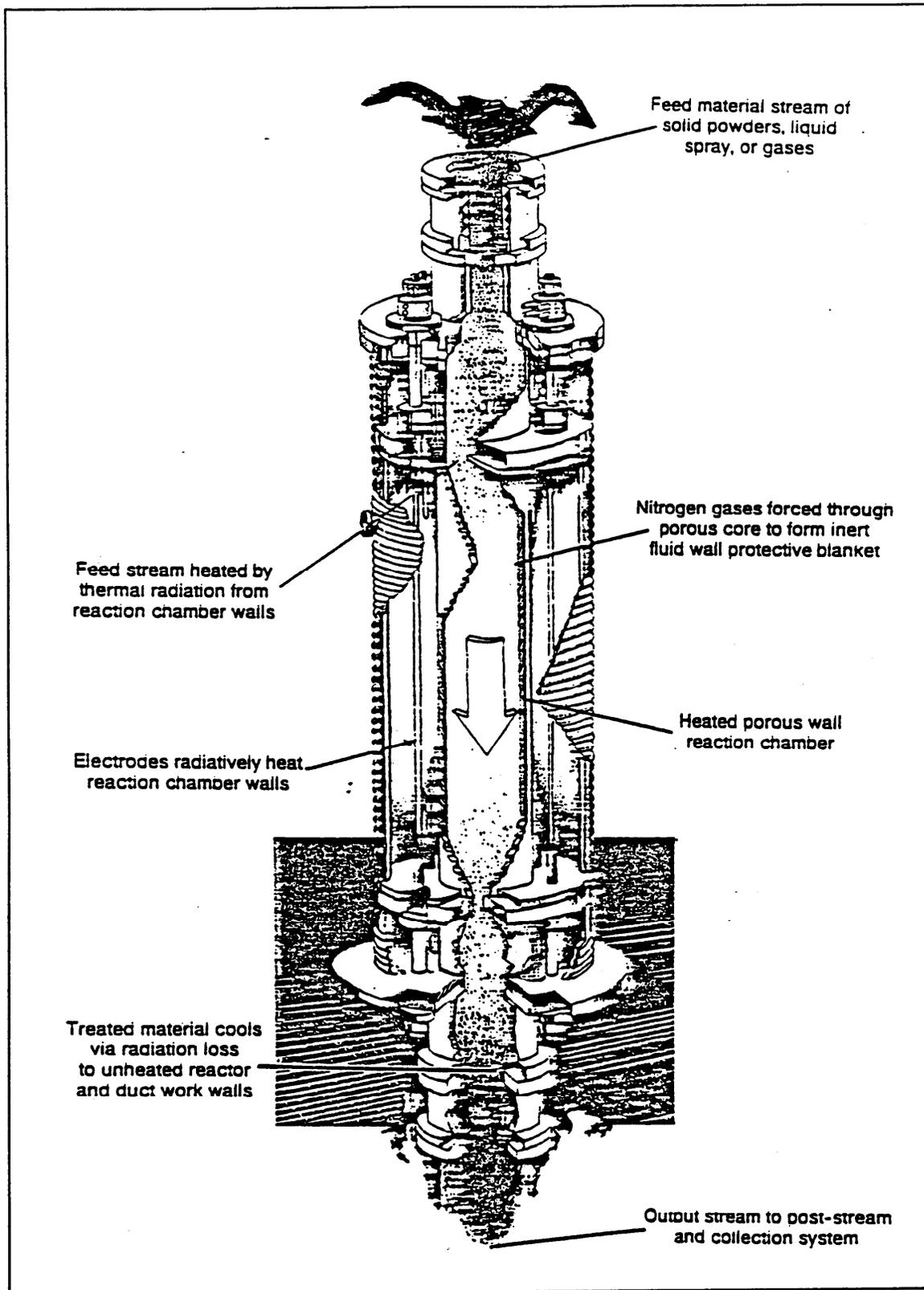


Figure 14. Vertical cross section of HTFW reactor (Source: J. M. Huber Corporation)

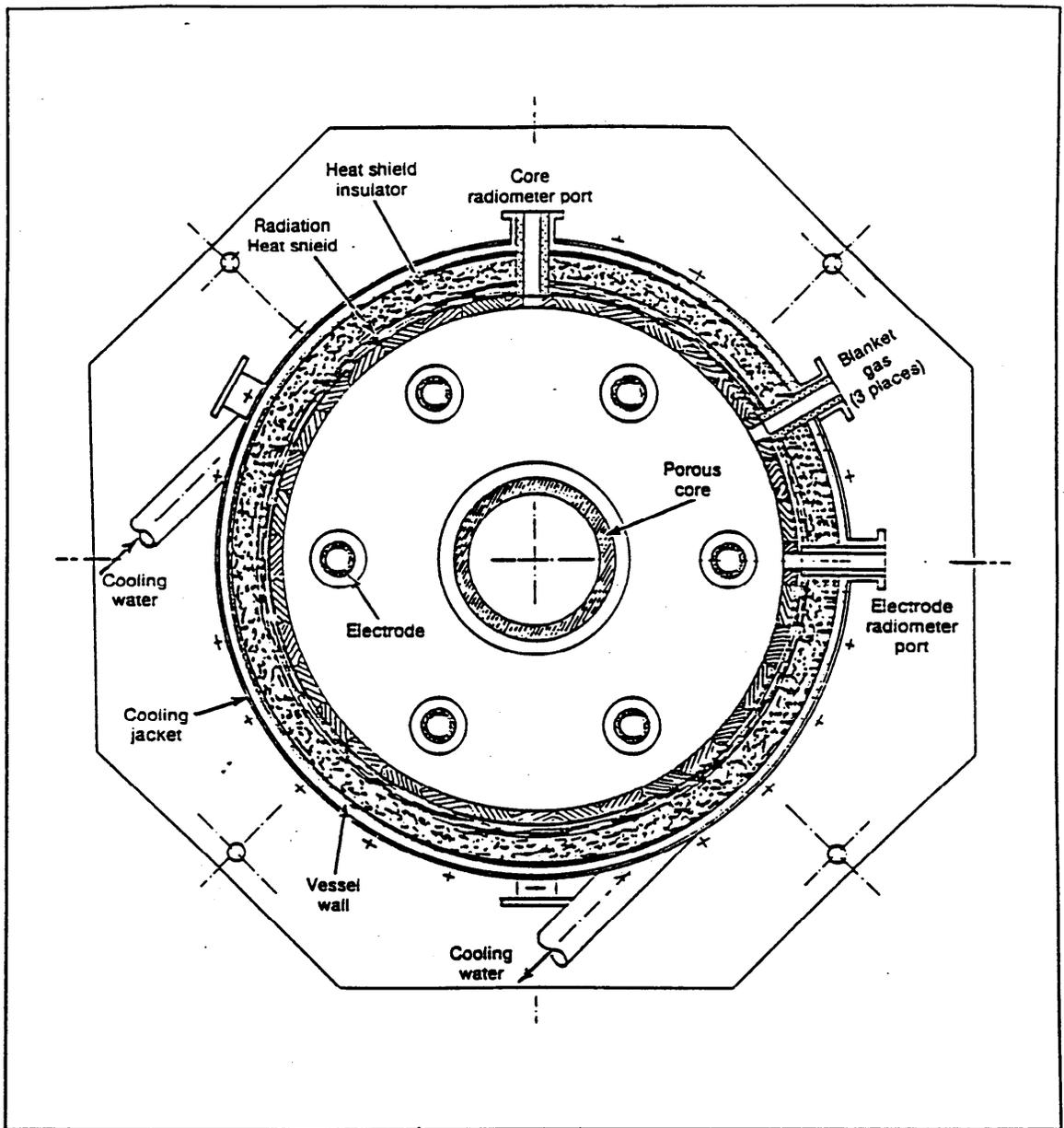


Figure 15. Horizontal cross section of HFTW reactor (Source: J. M. Huber Corporation)

into a nonleachable matrix, metals will leach out of this vitrified material under most conceivable long-term environmental conditions.

Residuals treatment/disposal requirements

For metals-contaminated soils, the vitrified (glassy) granular material containing the metals will require disposal. It is thought that this material will be nonhazardous and very stable, but this has not been confirmed for waste streams with high metals concentrations. If this material is nonhazardous, disposal or backfilling can be accomplished at low cost and low future risk. The disposal, however, is dependent on delisting, a typically lengthy regulatory process for each case.

The gases from the reactor must typically be treated prior to their being released to the atmosphere. If the phenomenon of vaporizing and subsequent recondensation of low-melting point metals is confirmed, disposal of baghouse dust as a hazardous waste will be necessary. The potential for dust recycling to the feed has not been addressed.

Adaptability

Several demonstrations have shown that the process can be used to treat soils contaminated with organics. Recent work has shown that soils contaminated with low levels of metals can be treated using this process to produce nonhazardous, vitrified residue.

Sludges and other residues may be similarly treated, if they are dried, reduced in size, and free flowing before input to the reactor.

Scale up potential

Test or commercial units are available to process 25 to 50 tons/day (Freeman, undated).

Potential disqualifiers

Principal concerns regarding application of the HTFW reactor are given below:

- a. High energy requirements.
- b. Disposal problems with baghouse dust.
- c. Hazardous gases may have to be treated to effectively remove metals.

- d. Particle size of feed is critical.
- e. Costs.

Roasting

Description

Most of the work in this area has been performed in Japan. As a result, there is limited information which is readily accessible on process performance. Reporting on the Japanese work focuses on treatment of heavy metal-contaminated dust or wastes (Kox and Van Der Vlist 1981).

The basic principle of this process is immobilization of the heavy metals in a vitrified or sintered form. As the waste material is heated, it passes through the following stages:

- a. Evaporation of the residual water.
- b. Decomposition of hydroxides and salts to form the corresponding oxides.
- c. Sintering, which is the fusing together of solid particles without reaching the liquid state, occurs at about two thirds of the melting temperatures ($^{\circ}\text{K}$).
- d. Melting of heavy metal oxides (around $2,000^{\circ}\text{C}$).

This process heats the waste to sintering temperatures where heavy metals are immobilized in the slag. X-ray diffraction photographs of the sintered slag show that the metals are in the dispersed phase while the silica melts to form the continuous phase. Since the objective of this process is immobilization, volatilization of metals should be prevented as far as possible. To achieve this, silicates in the form of clay minerals (i.e., kaolinite, sodium hydroxide, and ferric oxide) may be added to the melt, if these materials are not present in the waste or soils. This yields a more viscous melt, and the vaporization temperature of the metal compounds in the melt is reduced. Roasting of contaminated soils has not been studied, but naturally occurring silica in soils may provide the same benefit for soil treatment.

While research in this area has been conducted in Japan, no information is available to indicate that full-scale operations have been conducted. The probable furnaces would be either the rotary kiln or the Flammenkammer oven (Kox and Van Der Vlist 1981). Both these designs are capable of handling the molten slag. Some experimental data exist on the effect of additives and processing temperature on the leachability of slag derived from simulated metal hydroxide (electroplating) sludge. It has been shown that leachability decreases with increasing amounts of additives such as kaolinite

($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and increasing processing temperature. Organic waste components would be readily destroyed by combustion at the operating temperatures required.

Treatment effectiveness

There is no information regarding full-scale operations on soils contaminated with heavy metals. However, the experimental data that are available for simulated metal hydroxide sludge seem to indicate that the metals may be immobilized in a vitrified form and the glassy residue has very low leachability.

An appropriate mixture of additives (up to a 1:1 ratio) and temperatures from 1,000 to 1,200 °C were effective in reducing chromium leachate levels below 1 mg/L in both boiling water and weak acid (pH 5 with H_2SO_4) extractions. (Note that the melting and boiling points of chromium are 1,615 and 2,200 °C.) These extractions were apparently conducted to result in a 50:1 weight ratio of extract to treated waste in contrast to the 20:1 ratio for the TCLP (pH 5, acetic acid). These results indicate that leaching is limited to the surface of the slag and that TCLP targets can be achieved even for high-concentration (15 to 100 percent) chromium hydroxide sludges.

While no experimental data are available for soils, the natural mineral content and lower anticipated metals concentrations should make most soils a good potential substrate for treatment. Results are also not available in the literature for other hazardous metals.

Long-term stability performance

The glassy/vitrified residue is very stable and appears to leach metals only from its exposed surface area. It is expected that the long-term performance of the residue should be good, but long-term studies have not been conducted. Experimental data indicate that the leachability of the residue is not significantly affected by the pH of the solution and would not, therefore, be affected by anticipated environmental changes. The metals will still be contained in the soil, and thus susceptible to mechanical disturbance.

Residuals treatment/disposal requirements

If treatment can reduce the metals leachability below TCLP levels, the glassy/vitrified residue in which the metals are immobilized may be backfilled onsite or disposed in a nonsecure landfill. Off-gases from the process should be minimized by developing appropriate additives or modified gas scrubbing equipment for metals recovery, and any residue generated will require hazardous disposal and possible further treatment. These measures will be most

critical for metals such as arsenic and mercury, which volatilize at lower operating temperatures.

Adaptability

The roasting process effectively treats organics-contaminated soils and has potential for treating metals-contaminated soils. In fact, the literature suggests that, in cases where the waste includes metal contaminants, a rotary kiln soil incinerator can be modified to reduce the hazardous properties of the waste. This process has also been successfully tested for treating metal hydroxide sludges.

Scale up potential

The roasting process can be conducted in available rotary kiln incineration equipment. Therefore, scale up should be readily achievable.

Potential disqualifiers

Principal concerns regarding application of the roasting process are as follows:

- a. Lack of full-scale operational information.
- b. Control of hazardous (metals-containing) gases that may be emitted by the process.
- c. Delisting actions that may be required prior to disposing the slag as a nonhazardous waste.
- d. High energy costs.

Thermal Extraction (Chloride Volatilization)

Description

As with roasting technology, most of the work in this area has been performed by the Japanese, and only limited information is readily accessible. Heavy metals in the metal chloride form can be removed from the soil as a gas at high temperatures. This approach differs from roasting, in which the objective is to immobilize the metals in the vitrified residue.

Most metals occur in soil as oxides, much less volatile than the chlorides. Optimal treatment thus requires first converting the metal oxides to chlorides and then vaporizing them. These volatile compounds are reclaimed from the gas phase and treated or disposed in a suitable manner. In this process,

temperature and additives for chemical conversion to chlorides are critical factors. Additives are either chloride salts or other chlorine-containing materials that transform metal oxides to chlorides.

No full-scale operational data are available for this process. Japanese experimental data are available on the additives and temperatures used in the process. In one experiment, it was found that by adding CaCl_2 to sludge containing lead, cadmium, and zinc, 95-percent removal efficiencies were achieved at 1,100 °C (Kox and Van Vlist 1981). Another experiment involved the use of polyvinyl chloride (PVC) waste as an additive. The drawback with this method is that a minimum stoichiometric amount of PVC is required in the process. This results in the formation of HCl gas, which causes an air-pollution problem. This problem could potentially be solved by adding lime to bind the excess HCl and form CaCl_2 .

Treatment effectiveness

Experimental data show that the process cannot remove all the metals by volatilization. In one experiment, 95-percent removal efficiencies were demonstrated for wastes containing metals in the low-percent range.

Since the process cannot remove all the metals from the soil, the residue will still contain some metals. The experimental data for this particular waste show that, even with a removal efficiency of 95 percent, the residual metal concentration is about 0.1 percent. Although leaching data are unavailable, the mobility of residual metals depends upon the degree of vitrification achieved.

Long-term stability/performance

For treatments that produce total residual metals below compliance standards, the resulting waste will remain nonhazardous in the long term. On the other hand, high residual total metals concentrations present the potential for mobilization or leaching due to mechanical disturbance or severe environmental conditions.

Residuals treatment/disposal requirements

Volatilized metal chlorides must be cooled, condensed, and collected as a dust. Metal concentrations in the residue will be higher, but the leaching properties of the residue are unknown. Disposal requirements and costs would depend on leachability. Any HCl gas discharged, if PVC wastes are burned, will also have to be treated.

Adaptability

The process is conducted at high temperatures in rotary kiln-type equipment and is, therefore, also likely to successfully destroy organic compounds or explosives. With regard to metals treatment, the process has been shown at the experimental level to be applicable for treatment of metals-contaminated sludges but has not been demonstrated for contaminated soils.

Scale up potential

The process could be implemented using available solids mixing and rotary kiln incineration equipment. Therefore, scale up should be readily achievable.

Potential disqualifiers

Principal concerns associated with application of the thermal extraction process are listed below.

- a.* The process cannot remove all the metals from the soils. Thus, for high metals concentrations, treatment may not be effective.
- b.* Energy costs will be comparable to incineration and therefore may be prohibitive.
- c.* Residues from off-gas treatment may require hazardous disposal or further treatment.
- d.* Off-gas treatment costs may be high, especially when HCl has to be treated. New off-gas treatment technology is perhaps required.
- e.* Recovery of the volatilized heavy metal compounds from the gas phase may cause severe problems with respect to cooling, corrosion, and aerosol collection.
- f.* As with most extraction processes, the metals are removed from the soil, but other media are contaminated. These will require additional treatment. To be economical, processes must concentrate the metals in each step.

Plasma Arc (Metals Recovery)

Description

This technology has been applied on an experimental or pilot basis to address metallurgical process applications. Most of the research and development has been confined to metals smelting/melting, ore roasting, metals

calcining, chemical reactions/synthesis, and high-temperature gas heating. The impetus for these efforts in the late 1970s and early 1980s was the high cost of hydrocarbon fuels. The aim was to develop alternative energy-efficient technologies that use electricity. Some studies have been conducted on waste materials, primarily PCBs.

Several types of plasma arc systems are under investigation. The heart of all these systems is the plasma arc device (or torch). This device consists of a closely spaced pair of electrodes that are installed in a furnace and produce an electrical arc. A process gas is injected into the gap between the electrodes. This gas can be an inert, oxidizing, or reducing substance. The gas in and around the arc is activated into an ionized atomic state, absorbing large quantities of energy and losing electrons. The resulting gas is known as the plasma state (fourth state of matter), which consists of charged and neutral particles with an overall charge near zero and with electron temperatures up to 28,000 °C (Martin 1985; Freeman, undated). As the molecules or atoms relax from their highly activated state to lower energy levels, ultraviolet radiation is emitted.

Wastes are introduced into the reactive zone of the furnace where the molecular bonds of the waste material are broken as a result of the bombardment by electrons and high-intensity ultraviolet radiation. This results in the conversion of the waste materials to basic elements (e.g., carbon, hydrogen, oxygen) or simple molecules (i.e., carbon monoxide). The activated components of the plasma decay when their energy is transferred to the waste material. Hazardous gases that may emanate from the furnace must be scrubbed. Figures 16 and 17 show various configurations of plasma arc reactors and furnaces.

Performance data that are currently available for the plasma arc system are mainly for liquid wastes. The system has recently been tested for destruction of PCBs. Very limited information is available on treatment of soils contaminated with metals. However, the fact that the system has been used in recovery of metals from low-grade ores indicates that it may be used in certain instances for metals recovery from highly contaminated soils. In the treatment of ores, the plasma arc system is used as a heat source for smelting or primary reduction (i.e., to replace conventional blast furnaces). This process, when applied to soils with a mixture of metals, will result in a liquid melt and immobilization of metals, rather than oxidative destruction, as occurs with organics such as PCBs.

Treatment effectiveness

The literature indicates that no full-scale performance data exist for waste materials. Experimental data indicate that the system was effective in the destruction of PCB wastes (Lee, Schofield, and Lewis 1984).

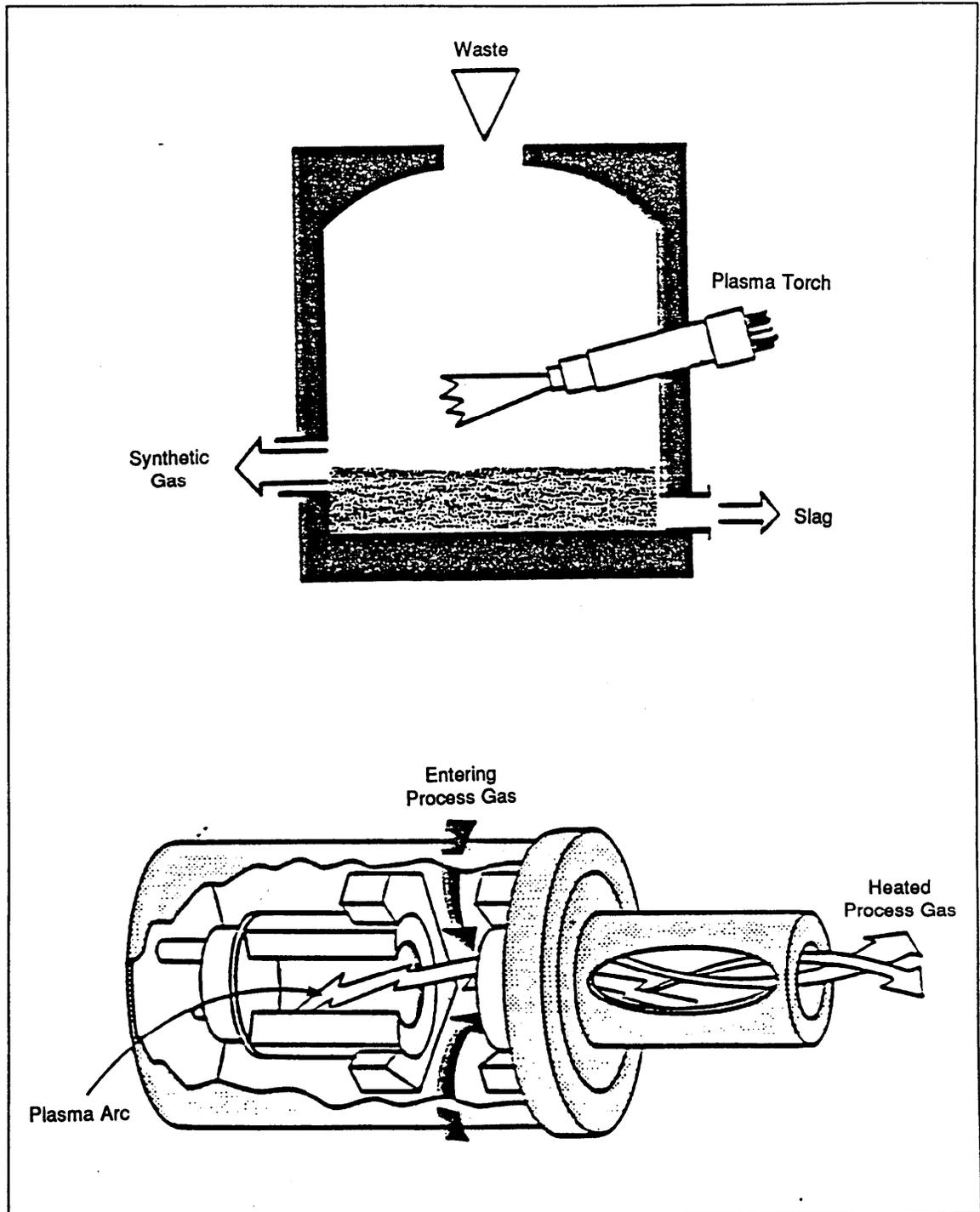


Figure 16. Schematic of plasma arc reactor (after Freeman, undated)

The work completed for metallurgical applications indicates that metals recovery is possible for high-concentration wastes. Success in processing ores indicates that soils can be readily handled by the equipment. The high silica and mineral content may affect operation and separation of metals. Based on

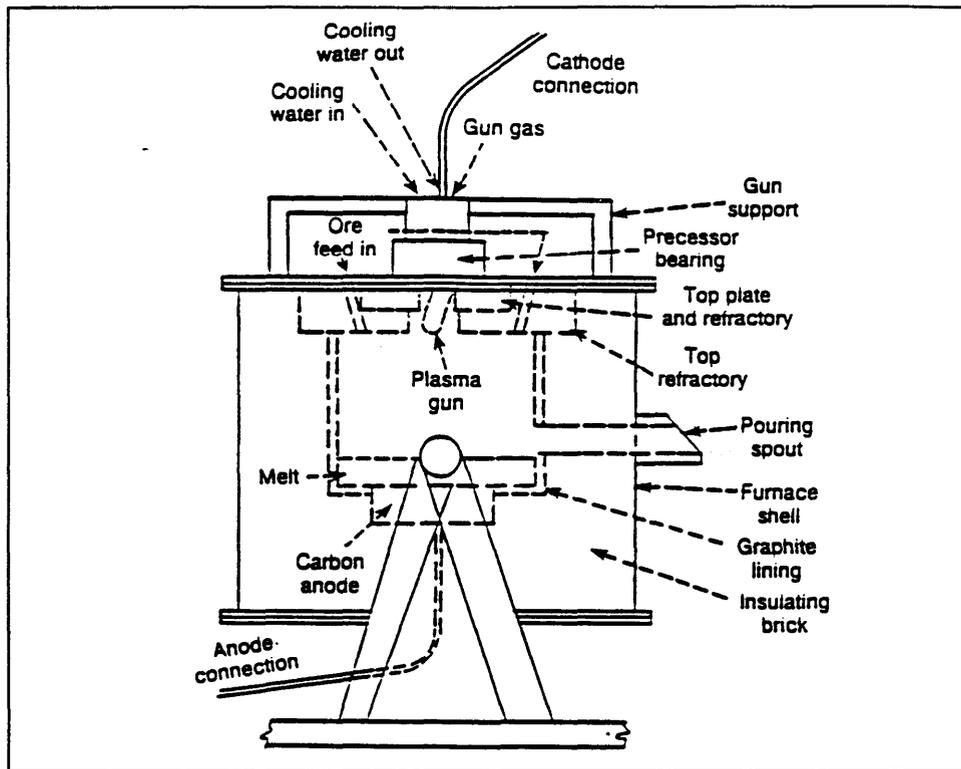


Figure 17. Cross section of plasma arc furnace (Source: J. M. Huber Corporation)

the high operating temperatures, the formation of a vitrified residue is likely. This residue may provide a nonleachable matrix for safe disposal.

Long-term stability/performance

Since the process essentially converts the waste components to basic elements, destruction of the organic waste is total. Therefore, any treated soil would be free of organic contaminants. Long-term performance for metals depends on the results from soil processing. If, for example, metals are recovered or trapped in a vitreous matrix, long-term stability is ensured.

Residuals treatment/disposal requirements

After the contaminants have been removed from the soils, the residual slag must be disposed. Slag leaching properties are as yet undetermined. The high temperatures will, however, result in a high level of metals in the off-gases passing onto the dust collectors. These metals will be primarily, but not exclusively, the more volatile metals, such as mercury and arsenic. This dust may require disposal as a hazardous residue. As noted in the section on the HTFW reactor (see Chapter 3), substantial metals are also likely to escape baghouse

capture. Scrubbers may be used to treat the hazardous gases, but effectiveness is uncertain. No data for metals-contaminated soils are available at this time.

Adaptability

Tests have clearly shown that the process can be used to treat organic wastes. Soils contaminated with organics may be successfully treated by the process. Sludges and other waste materials may also be treated, but data are limited.

Scale up potential

Tests have been conducted for wastes in a pilot unit sized for 500 lb/hr of sludge. Based on metallurgical studies and applications, scale up should be achievable.

Potential disqualifiers

Principal concerns regarding application of the plasma arc process are as follows:

- a.* Energy cost is an important factor in determining the economic feasibility of the process.
- b.* Plasma arc technology has been attractive in metallurgical applications only where poor heat utilization and high cost occur for fossil fuels as compared with electricity applied via plasma arc. In recent years, the cost advantage for electricity has disappeared, and interest in plasma arc has also declined.
- c.* Literature indicates that the capital and operating costs (based on a pilot-scale test) will be high.
- d.* In addition, off-gases will require treatment. Baghouse dusts and/or bottom ash may be listed as hazardous waste and treated or disposed accordingly.
- e.* The soil will probably be vitrified, but data are not available. The vitrified soil would probably be stable, but metals will still be present and subject to mechanical disturbance and mobilization.

Vitrification

In situ vitrification

Description. In situ vitrification (ISV) is a process of immobilizing the contaminants in soil by converting the soil into a stable glass and crystalline form that has chemical durability properties similar to those of obsidian. This is an emerging technology that has been extensively tested and developed by the Battelle Pacific Northwest Laboratory (under contract to the U.S. Department of Energy) on soils contaminated with radioactive materials (Buel, Fitzpatrick, and Timmerman 1985). Battelle's scientists claim that, while the technology "is not a panacea for all contaminated soils," it does have the following advantages (Buel, Fitzpatrick, and Timmerman 1985):

- a. Long-term stabilization of radioactivity (>10,000 years).
- b. Cost effectiveness (\$122 to \$252/cu yd).
- c. Applicability to varying soil and site conditions.
- d. Minimal occupational exposure to the waste during processing.
- e. Low energy requirements (<0.5 kW/lb).

The ISV process is initiated by inserting molybdenum or graphite electrodes into the soil in a square grid pattern. The spacing of the electrodes varies with the size of the ISV unit (e.g., 0.23 to 0.36 m for an engineering unit; 3.5 to 5.5 m for a large-scale unit). Next, a conductive mixture of flaked graphite and glass frit is placed in an X pattern among the electrodes in 5-cm-deep trenches on the soil surface to initiate electrical conductance. Voltage is then applied to the electrodes via a power source (as much as 4,160 V for the large-scale unit). The graphite mixture is quickly heated to soil-melting temperature (1,100 to 1,600 °C). As the surrounding soil melts, it becomes electrically conductive. The graphite is eventually consumed by oxidation, and the molten soil maintains the electric conductivity (Buel, Fitzpatrick, and Timmerman 1985; Martin 1985).

Figure 18 illustrates how the molten soil zone grows outward and downward as the process progresses and eventually encompasses the volume between the four electrodes (Buel, Fitzpatrick, and Timmerman 1985). As the temperatures in the molten zone approach 2,000 °C, organic wastes in the soil are pyrolyzed. The resulting gases from the process burn when they come into contact with the air. The high temperatures and long residence times result in essentially complete combustion and/or destruction of the organic components. Many of the nonvolatile and semivolatile elements at these temperatures, such as heavy metals, remain in the molten glass and become part of the glass and crystalline product after cooling. The percentage of hazardous elements that

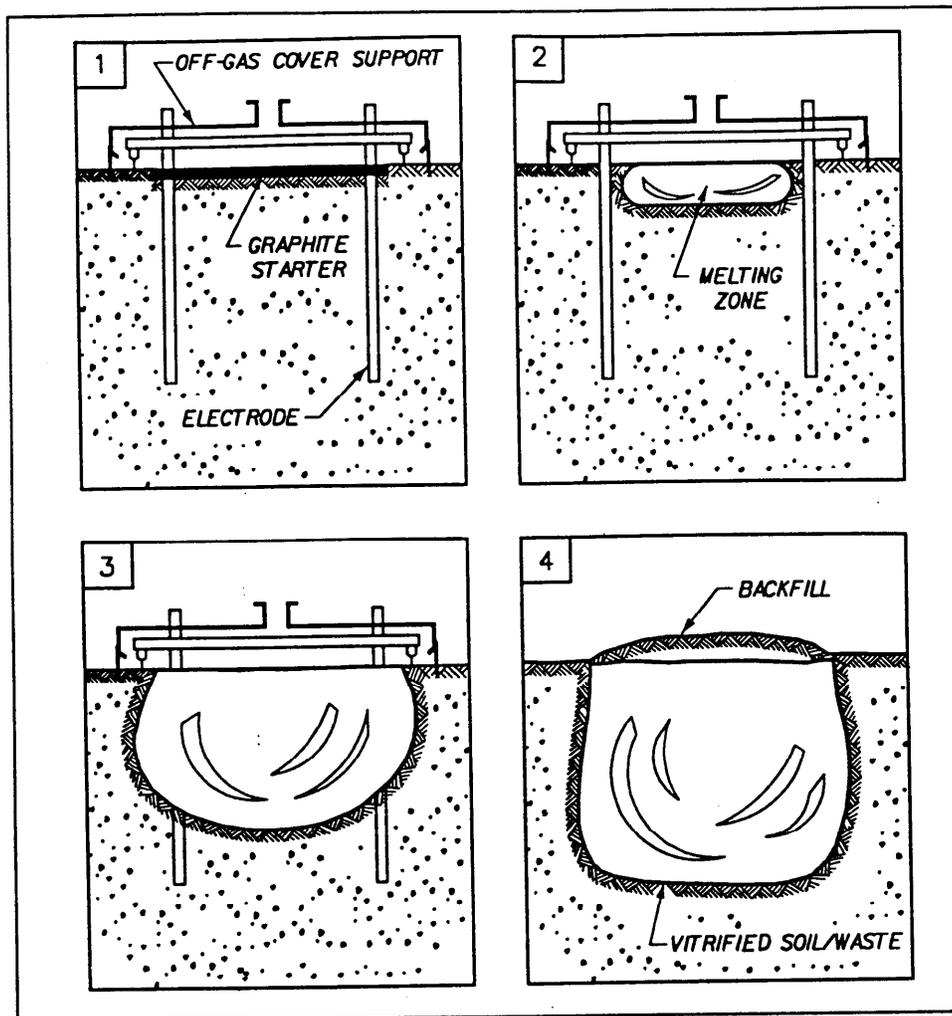


Figure 18. Process sequence of in situ vitrification (after Buelt, Fitzpatrick, and Timmerman 1985)

escapes can be collected by an off-gas hood that is placed over the vitrified zone. The off-gas is then treated in a treatment system, which is housed in a mobile unit, as shown in Figure 19. Thus, the process is self-contained and transportable.

When the desired vitrification depth is attained, voltage to the electrodes is discontinued, and the molten mass is allowed to cool. The entire cooling process can take several months, depending on the size of the vitreous mass produced, but this does not interfere with the use of the power system and off-gas treatment for additional settings. After the surface of the molten glass has cooled, the vitreous mass is backfilled with clean fill, because of a reduction in volume upon treatment.

Treatment effectiveness. Literature indicates that the effectiveness of the ISV process has been demonstrated over a range of site sizes. As indicated previously, most of these tests have been done on radioactive contaminated

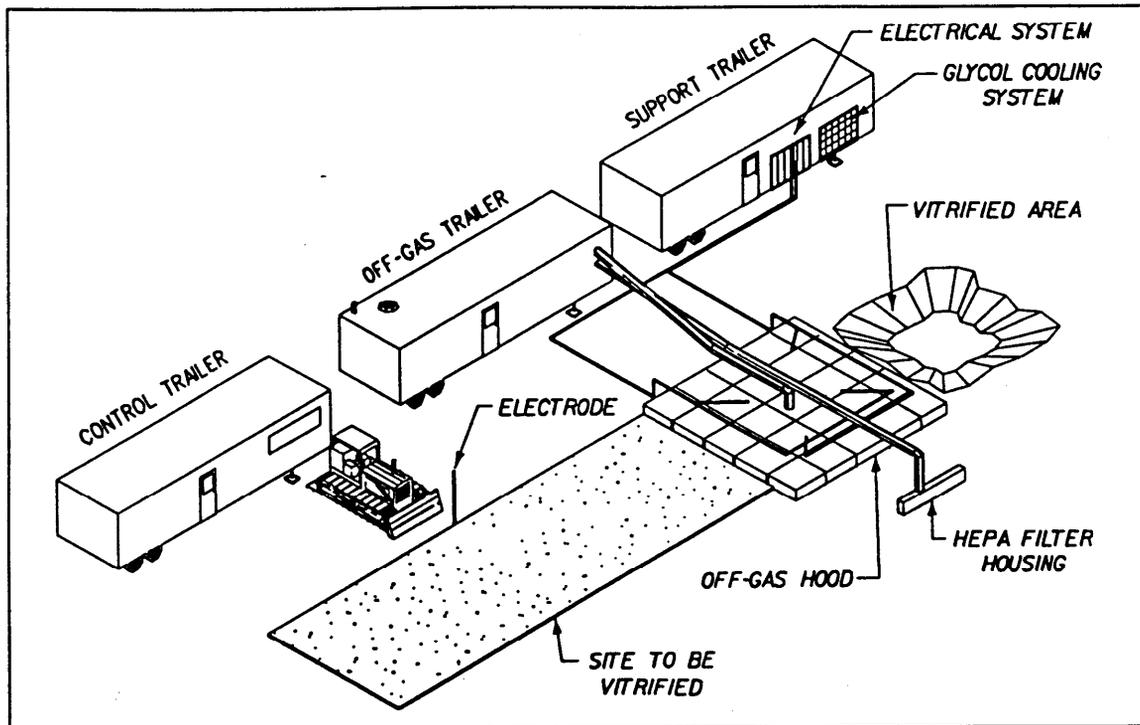


Figure 19. Large-scale testing unit (after Buel, Fitzpatrick, and Timmerman 1985)

soils where concern for mobility is more acute than for metals. The leachability of metals following vitrification is expected to be negligible.

Recently, four large-scale tests (300- to 500-metric ton blocks) have been completed in the initial phase of operational acceptance testing of the large-scale equipment. All test data appear to show that the technology can be used on different types of soils. Soil moisture requires a significant expenditure of energy to accomplish vitrification, because of its high heat of vaporization.

As stated, the molten zone would encompass the area between all the four electrodes. Depth of the zone ranges from 2 to 13 m. Metal objects such as pipes and bars can short out opposing pairs of electrodes, preventing heat from being dissipated into the melt. However, test results show that the ISV process can accommodate metal objects occupying up to 70 percent of the spacing between the electrodes (Buel, Fitzpatrick, and Timmerman 1985).

Long-term stability/performance. Once glassification is achieved, the amorphous glass product of ISV treatment is a low-permeability, low-metals mobility matrix that is thought to be extremely stable over time (>10,000 years). Geologic stresses are expected to cause fractures such as those that occur in bedrock, which would cause secondary hydraulic permeability. The low metals mobility and low-fracture surface areas should provide relatively permanent treatment effectiveness.

Residuals treatment/disposal requirements. One of the inherent advantages of the ISV process is that no hazardous residual must be disposed. The gaseous effluent can be treated in a mobile off-gas treatment unit. However, more volatile metals may evolve, requiring treatment other than that provided for organic volatiles. The vitrified soil remains in place. Land reclamation and reuse may be limited by the physical properties (hardness, low permeability).

Adaptability. Though most of the testing has been confined to radioactive-contaminated soil, there is some information on organic-contaminated soils. Conclusions from these tests (Buelt, Fitzpatrick, and Timmerman 1985; Martin 1985) are summarized below.

- a. Burial depth attenuates release of hazardous elements (e.g., a meter of uncontaminated overburden lowers release fractions significantly).
- b. Gaseous releases associated with combustibles result in significantly higher release fractions.
- c. Organics are pyrolyzed in the soil-melting process at high temperatures, resulting in essentially complete combustion in the hood directly above the molten zone.

Communications with Battelle indicated that the process can also be adapted to sludges or other waste materials either in situ (if waste is in-ground) or in aboveground process equipment (see following section, Aboveground vitrification). While ISV could be used on residues from organic treatment processes, it can be used alone to treat for both organics and metals.

Scale up potential. ISV has been demonstrated in field tests treating a soil cube approximately 20 ft on each end. The process requires 2 to 3 days to complete. Thus, throughput rate for this transportable system is 100 to 150 cu yd per day. Higher rates would require multiple units operating on the site.

Potential disqualifiers. Principal concerns regarding application of in situ vitrification are as follows:

- a. Safety may be a concern because of the use of high-voltage power and the release of volatile organics and inorganics to the air.
- b. Air emission controls are included in process design. Based on testing and projections, problems of safety, release to the environment, and air emissions are controllable. Special gas treatment may be required for emission of certain hazardous substances.
- c. Metal objects may short out the current distribution, resulting in poor treatment.

Aboveground vitrification

Description. Conventional glass-making techniques have been adapted in this process to pyrolyze and oxidize or fuse wastes with molten glass to form a residue that is nonleachable. Soils containing glass minerals may be readily vitrified with minor additions of glassifying agents. Two firms are developing or marketing this process:

- a. Battelle Northwest-Joule-Heated Glass Melter.
- b. Penberthy Electromelt International-Electromelt Pyro-Converter.

The process was initially studied for long-term isolation of radioactive wastes and is now being applied to hazardous wastes and site remediation.

Battelle's process uses the material being heated as the resistance element in an electrical circuit without transferring heat from a metallic resistance element. Contaminated soils may be accepted directly with little or no pre-treatment. Organic constituents would be destroyed by pyrolysis and/or combusted at the operating temperature of 1,200 °C, while inorganic constituents (including nonvolatile heavy metals) would react with glass formers to create an impermeable glass matrix. Molten glass from the melter is continuously drained into an inexpensive receiving canister and cooled to ambient temperature. These canisters may be disposed of in a nonsecure landfill if regulatory criteria are met. Battelle claims that the glass residue is in itself a long-term disposal medium, exhibiting leaching properties similar to Pyrex or granite. Off-gases from the melter will include pyrolysis products from organics and volatile inorganics (e.g., heavy metals requiring measurement), which will require additional treatment (Freeman, undated). Organic pyrolysis gases combust upon leaving the melt when provided adequate oxygen.

In the Penberthy process, waste is directly charged into a pool of molten glass, also heated in an electric furnace (Penberthy 1986). Again, this results in the organic constituents being destroyed by pyrolysis and pyrolysis gas combustion, while the inorganic constituents mix with the molten glass to form a nonleachable residue. The residue is drained into canisters for disposal in a nonsecure landfill, again, assuming delisting. This process has been successfully tested using a number of wastes. The company has one pilot-scale unit at Seattle, WA, and another experimental unit at a Monsanto facility in Ohio used to process transuranic wastes.¹ Numerous alternative configurations are offered in sales literature, including a rotary kiln primary treatment step followed by the standard furnace with molten glass at the base to "capture dust particles" and provide secondary combustion. Options described for air emission control include limestone rock-packed tower, wet scrubbing, and mist elimination. The entire system is maintained under negative pressure by

¹ Personal Communication, 1986 (Jul), Dennis Hotaling, Technical Manager, Penberthy Electromelt International, Seattle, WA.

means of an exhaust blower. Figure 20 shows a schematic diagram of the basic process.

Battelle's process is still at an early developmental stage. However, the Penberthy process has been tested on organic wastes and has proven successful. Penberthy is in a good position to commercialize this process, based on the pilot-scale test results and their extensive experience in glass-making equipment.

Treatment effectiveness. The vitrification process has been shown in studies to produce an extremely stable, nonleachable product.

Long-term stability/performance. The glassy residue that is formed contains the inorganic constituents (including heavy metals) and is very stable. Leaching characteristics of this glassy residue are similar to those of Pyrex and granite. It will be stable under all anticipated environmental conditions.

Residuals treatment/disposal requirements. If the metals are not leachable and the residue meets specific regulatory criteria, this residue may be disposed or backfilled with no special precautions. In some cases, beneficial reuse may be possible. Off-gas from the process will require treatment. This is especially critical for instances in which volatile metals (e.g., mercury, arsenic) or chlorinated organics are present in the waste. Additives to reduce volatilization, as discussed for roasting technology, have not been explored for off-gas treatment. After cooling, metals may be collected as dust and recycled (revolatilized) to the melt if the fraction remaining in the melt is high enough.

Adaptability. The ability of this process to handle organic wastes in combination with metals has been demonstrated. No pretreatment for organics destruction would be required. The system can also readily handle liquid wastes and sludges. In these cases, the addition of glass-forming raw materials will be necessary.

Scale up potential. While the Battelle process remains developmental, Penberthy equipment is reportedly available to process up to 4,000 lb/hr or 48 tons/day (Freeman, undated). Penberthy promotional literature indicates that units could be sized to process up to 25,000 lb/hr or 300 tons/day.

Potential disqualifiers. Principal concerns regarding application of aboveground vitrification are as follows:

- a. The costs associated with the application of this process to the treatment of metals-contaminated soils appear to be somewhat high. Penberthy estimates that for a 2,000 lb/hr feed of tetrachlorobenzene or similar substance, the capital costs would be \$1 million and the operating cost would be \$100/ton of feed. It must be noted that this estimate is based on organic waste that is readily combustible. The

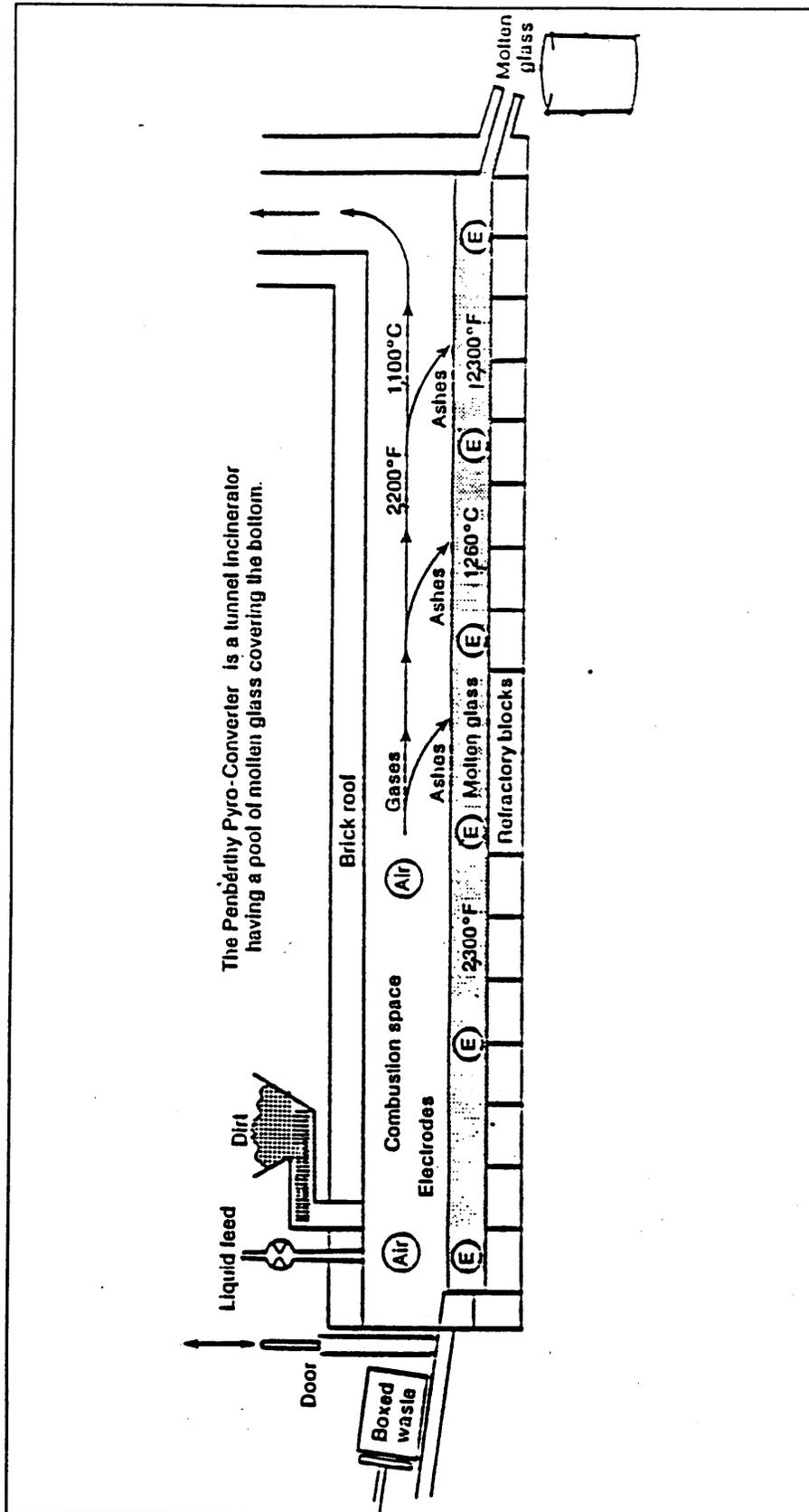
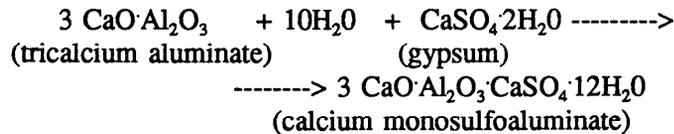
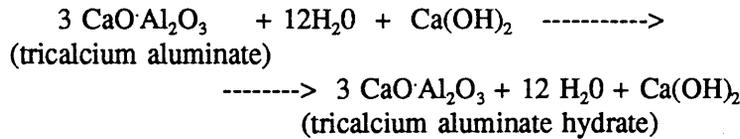
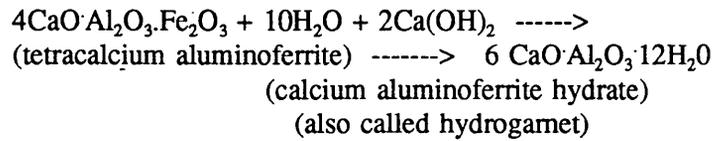
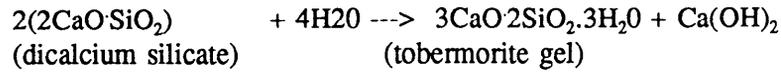


Figure 20. Penberthy Pyro-Converter (from Freeman, undated)

cost may be significantly higher for soils contaminated with heavy metals.

- b.* Backfilling will be required to compensate for reduced volume of the vitrified soil.
- c.* Metals would be fixed in the vitrified soil. Leaching potential would be low. However, the metals would still be present and subject to mechanical disturbance or mobilization, and delisting actions may be necessary.
- d.* Additionally, off-gas treatment may be expensive, especially in instances where volatile metals are present in the soil. The potential technical problems all appear to be manageable, however.



As mentioned previously, several commercial processes have been developed. These processes differ in the use of proprietary additives to enhance immobilization of contaminants in the waste.

- (2) Typically, S/S is applied as follows. Soils from sites contaminated with metals would first be excavated and slurried with water (if necessary). Cement and other additives would then be mixed with the soil slurry. The resultant mixture sets to form a hardened mass. Specific process parameters, such as the amount of water required, cement formulation requirements, etc., must be determined for each soil based upon site-specific conditions. Figure 21 shows a process flow diagram for the commercial Soilroc Process. The type of cement used depends on type of waste, e.g., Type I - normal cement used in construction; Type III - high early strength, recommended for use where rapid set is required; and Type V - special low-alumina, sulfate-resistant cement, recommended for high-sulfate content (>1,500 mg/kg) waste (Mahoney et al. 1981). This process can be used in a batch or continuous mode. Advantages of this process include
 - (a) The moderate price of additives.
 - (b) Availability of processing equipment.
 - (c) Proven ability of the process to immobilize metals.
- (3) Some of the disadvantages of using this process are as follows:
 - (a) Since metals remain in the treated soil, the potential for their leaching is always present.

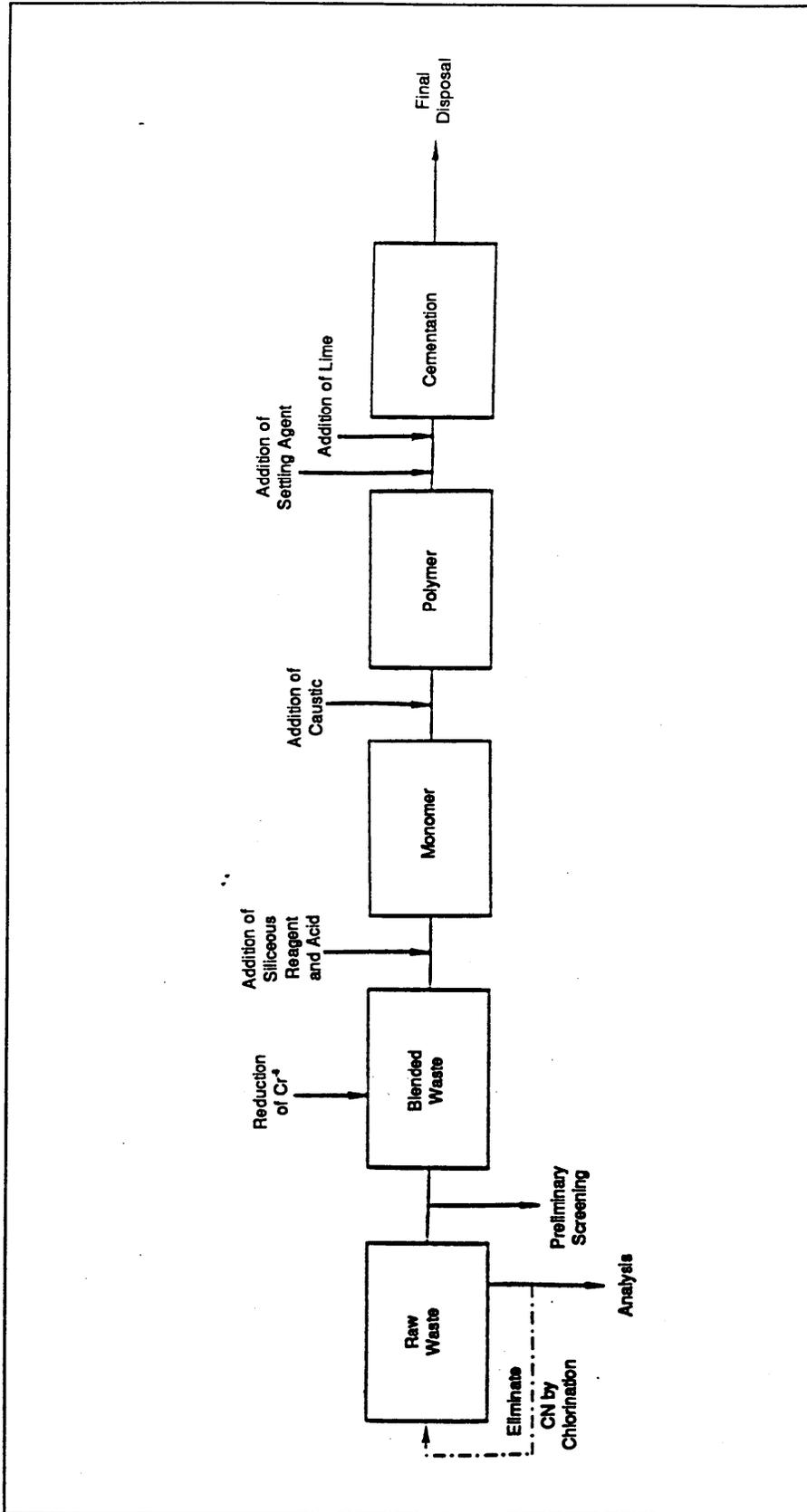


Figure 21. Flow diagram for Soilroc process (from Rousseaux and Craig 1981)

- b. *Lime-based techniques.* These techniques make use of the reaction of lime with silica and water to form a hard, concrete like material, often called pozzolanic concrete. Additives such as fly ash, cement-kiln dust, and other (possibly proprietary) materials are added to the process to increase the strength of the S/S waste or to retard the migration of the contaminants (Pojasek 1978).

As in the cement-based techniques, there are several commercial processes that use various additives to form pozzolanic materials. Figure 22 shows a process flow diagram for the Envirosafe process used to treat sludges and liquid wastes. Adding lime to the waste results in the pH being raised, which generally reduces the solubility of metals. Adsorption and ion exchange are also enhanced by the pozzolanic reactant and products. Soil with metal contaminants is mixed and treated with the pozzolanic reactants to yield S/S material that can be land-filled. The advantages of this process include low costs for additives and ease of operation of processing equipment. One of the disadvantages of this process is that the treated material is susceptible to attack by acidic solutions (Mahoney et al. 1981).

Treatment effectiveness

The ability of S/S processes to effectively immobilize metals in liquid wastes and sludges has been demonstrated at all levels--experimental, pilot-scale, and field operational (Pojasek 1978, 1980; Smith 1979; Mahoney et al. 1981; Rousseaux and Craig 1981; U.S. Army Armament Research and Development Center 1982, 1986; Zenobia and Smith 1982). Based on the available literature, soils contaminated with low levels of nonvolatile organics may also be effectively treated using these processes. The choice of the type of process will depend on the site-specific conditions. Tables 2 and 3 show the effectiveness of the Soilroc and Envirosafe processes in immobilizing metals and meeting regulatory limits. Table 3 illustrates that several environmental concerns, such as oil and grease and total organic carbon (TOC), are reduced by this process. This is significant for the treatment of mixtures of organic and metal contaminants.

Long-term stability/performance

The S/S material that is formed by the process should be stable over the long term. Leachate tests that have been performed on these materials have shown that the extract contained metal concentrations below the USEPA's Extraction Procedure toxicity limits and Toxicity Characteristics Leaching Procedure (U.S. Army Armament Research and Development Center 1982, 1986; Zenobia and Smith 1982). When the treated waste is tested for EP toxicity, the pH remains above 7, maintaining stability. Severe, highly acidic conditions can destabilize the material, but these conditions are not expected in

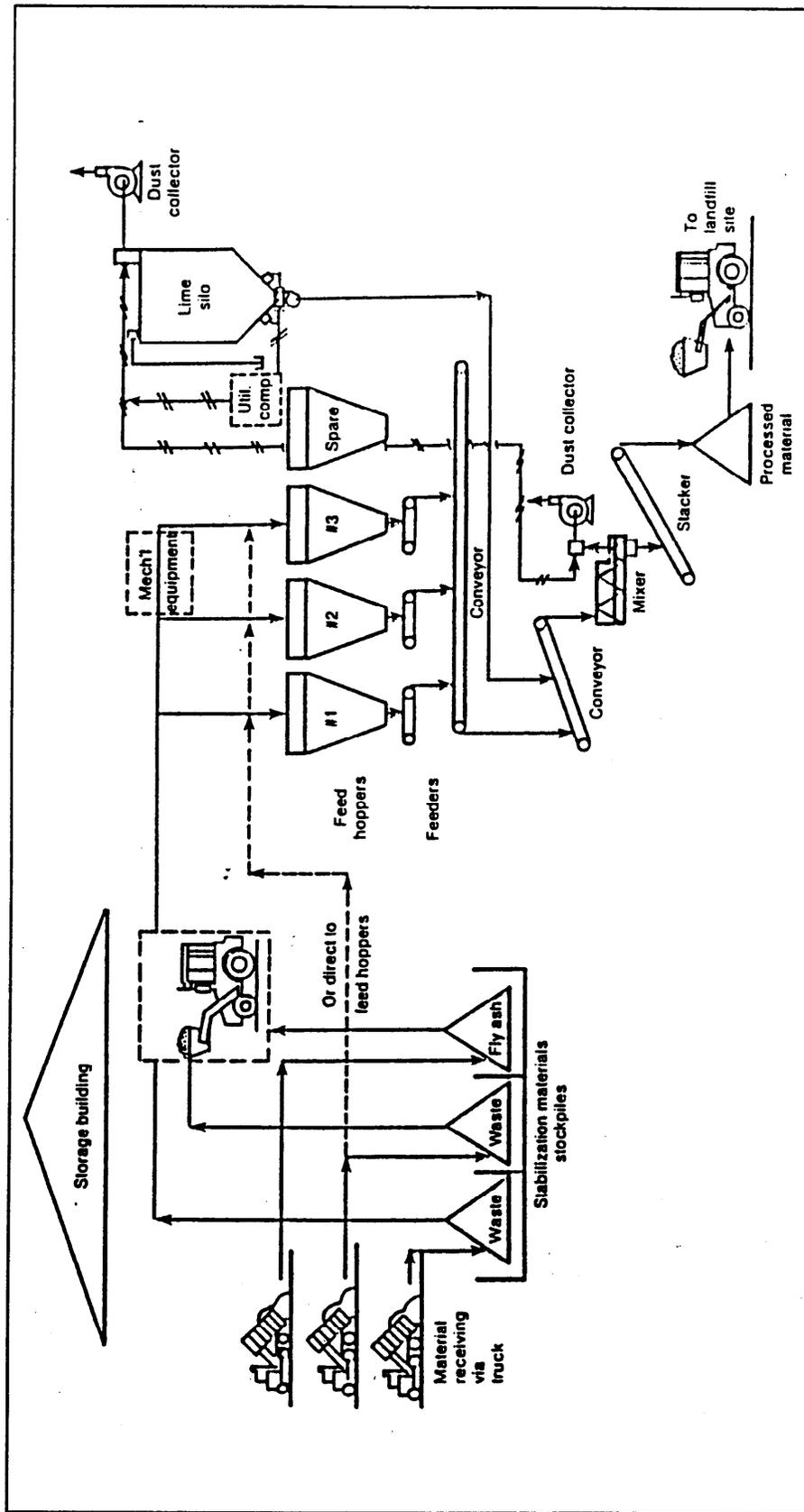


Figure 22. Flow diagram for Enviro-safe process (from Zenobia and Smith 1982)

Table 2 Comparison of Raw Waste Metal Concentrations with EP Toxicity Concentrations After Stabilization by Solliroc Process								
Sample No.	pH	CN mg/L	Metals					
			Cd	Cr	Cu	Ni ¹	Pb	Zn
Analytical Results of Raw Waste Samples²								
1	1.0	1.27	15,400	57,000	450	305	4.00	180
2	13.0	2,430	910	535	1,850	5,800	0.74	5,400
5	10.1	968	782	3,890	25,500	1,330	2,000	28,700
6	13.2	33.7	35.2	440	13,800	5,660	6,580	5,030
7	<1.0		53.0	470	39.0	46.0	³	5,000
Analytical Results of EP Extracts⁴								
1		⁵	5.60	0.10	0.28	1.30	0.013	34.8
2		⁵	2.30	0.27	0.64	0.95	0.016	5.00
4		⁵	0.10	0.13	0.06	0.15	0.006	0.41
5		⁵	2.70	0.18	0.36	1.15	0.017	25.0
6		⁵	<0.01	0.50	0.05	<0.10	0.008	0.50
Maximum Allowable Concentration								
			1.0 ⁶	5.0 ⁶	100 ⁷		5.0 ⁶	500 ⁷
<p>Source: Rousseaux and Craig (1981).</p> <p>¹ Nickel is not regulated by the primary or secondary drinking water standards.</p> <p>² Metal concentrations are given in units of µg/g (wet weight of sludge), as received.</p> <p>³ Analysis not performed.</p> <p>⁴ Metal concentrations are expressed as mg/L.</p> <p>⁵ Cyanide removed by pretreatment with H₂SO₄ pickling liquor.</p> <p>⁶ RCRA-TCLP levels.</p> <p>⁷ 100 times the secondary maximum contaminant level.</p>								

the environment. Furthermore, the S/S product has a low permeability and high strength. This should further improve performance over that indicated by the TCLP, based on a sample crushed to less than 9.5 mm (Bricka, Holmes, and Cullinane 1992).

Residuals treatment/disposal requirements

The S/S product containing the immobilized metals must be disposed in an appropriate manner. Depending upon the nature of the soils, metals concentration, and stabilization performance, the stabilized product may have to be classified/delisted prior to ultimate disposal as a nonhazardous waste. The usual mode of disposal is landfilling. In some cases, however, the

Table 3 Comparison of Chemical and Physical Characteristics of Wastes Successfully Stabilized by Envirosafe Process			
Parameter	Raw Waste DWB ¹ mg/kg	Stabilized Waste	
		ASTM Method A Leachate Analysis ppm	RCRA Standards ppm
Chemical Characteristics			
Total solids	99.8		
TOC	840	30	
pH	11.8	11.6	
Oil/grease	479	12	
Ag	235	0.05	5.0
As	34	0.01	5.0
Ba	10	0.75	100
Cd	1,680	0.01	1.0
Cr	1,155	0.15	5.0
Hg	2.8	0.2	0.2
Pb	49,600	5	5.0
Se	2.0	0.07	1.0
Physical Characteristics			
Unconfined compressive strength (cured 7 days @ 100 °F)		>100 psi	
Unconfined compressive strength (cured 28 days @ 73 °F)		>150 psi	
Permeability		1 x 10 ⁻⁵ cm/sec	
Source: Zenobia and Smith (1982). Note: Comparison based on use of Envirosafe process with a generator (as for typical steel corporation) and the resultant waste (air pollution control residue and electric furnace dust). ¹ Dry weight basis.			

high-strength, nonhazardous S/S product can be used for construction materials.

Adaptability

The ability of the process to handle liquid wastes and sludges has been well established. In some cases, residues from organic contaminants have also been treated. The application of S/S is site and waste specific.

Scale up potential

The process is in full-scale commercial use. Conventional batch or continuous-feed and mixing equipment may be used. Large capacity can be achieved by increasing equipment sizing or utilizing parallel process lines.

Potential disqualifiers

Principal concerns associated with stabilization/solidification are as follows:

- a. Organic wastes interfere with the process.
- b. Low-binder to waste cement and pozzolanic cement products are susceptible to attack by highly acidic solutions.
- c. Contaminants are not removed. The potential for mechanical disturbance and/or leaching, while reduced by S/S, is still present.
- d. Long-term performance is not understood.

Microencapsulation

Description

In this process, contaminant particles in solid or liquid waste are immobilized by encapsulation materials that create small-scale encapsulation cells. Metals-contaminated soils would be excavated and mixed with a polymeric substance in an extruder to form a product in which the contaminants are encased in a polymer matrix that is dispersed throughout the soil. Immobilizing materials (which form the matrix) may include polymers such as polyethylene and other thermoplastics such as asphalt bitumen.

The SEALOSAFE process is a commercial full-scale method used to treat wastes. This process is operated under the trade name STABLEX. Chappell and Willetts (1980) have reviewed test data on independent tests to verify the manufacturer's claim that the process effectively isolates heavy metals. The process consists of first pretreating the waste to form a homogenized product. Pretreatment includes neutralization of acidic wastes by waste alkalis, reducing Cr^{6+} to Cr^{3+} by treating the waste with spent acid, and other processes as necessary. The pretreated waste is then thoroughly mixed with a monomer and subjected to polymerization to form a slurry that later (after 3 days) hardens to form a rocklike material. Leachability tests (under worst-case conditions of grinding the product and subjecting it to an acid solution), conducted in the United States, United Kingdom, and Japan, showed that the leachate contained very low concentrations (<1 ppm total) of metal (Chappell and Willetts 1980). The permeability of the product is less than that of clays or concrete. The encapsulation materials are proprietary, and thus cannot be described.

Another immobilizing agent used to microencapsulate contaminants is asphalt. Brenner and Rugg (1982) investigated the effectiveness of using asphalt and asphalt/sulfur blends to encapsulate metals. In their experiments, molten sulfur and liquefied asphalt were first mixed for 8 min to form an emulsion at a temperature between 285 °F and 300 °F. This emulsion was then immediately mixed for 2 min with a preheated "simulated" waste similar to copper sulfate, at a temperature between 290 °F and 305 °F. A variation in this process (mixing the solid waste in the asphalt and then mixing it with sulfur) proved to be preferable because it yielded more uniform product. Their results showed that the best results, in terms of binding, were achieved when a ratio of 60 percent waste and 40 percent binder (asphalt and sulfur) was used. The tests also showed that the product exhibited strong resistance to chemical and mechanical stresses. Minor problems with increased leachate due to partially encapsulated particles were solved with the application of a thin exterior coating of asphalt by hot spray or dipping. Brenner and Rugg (1982) emphasized that their findings are applicable only to the experimental wastes they used and that waste-loading capacities may actually be higher for actual wastes used in a full-scale process. They also reported in 1982 that the estimated costs (excluding amortization) of treatment using a sulfur/asphalt blend would vary from \$41 to \$45/ton (for a 50-ton waste/week plant) to \$42 to \$44/ton for a 25-ton waste/week plant) (waste solids = 60 percent by weight) (Brenner and Rugg 1982). This cost does not include excavation and/or disposal.

Brenner and Rugg (1982) also state that this process has been implemented on a full-scale level and is called the Volume Reduction and Solidification System (VRS). This full-scale VRS process is nonchemical and uses an extruder that simultaneously evaporates water from the waste while mixing it into the asphalt binder. The homogenized waste/asphalt mix is then discharged into containers, where the mix cools. Upon cooling, the volume of the waste/asphalt mix is reduced considerably. Figure 23 shows a process flow diagram for the VRS process.

A process, described in the following subsection, combines microencapsulation with macroencapsulation. This process, developed by Environmental Protection Polymers, uses 1,2 polybutadiene and polyethylene to coat the particles of soil or waste and to form a structural block. The block is then coated with high-density polyethylene (HDPE, macroencapsulated) before disposal (Lubowitz and Wiles 1981).

Another process involves the use of an organic polymer-modified gypsum cement called Envirostone Cement, manufactured by U.S. Gypsum Company. This process is a modified cement stabilization process, that combines inorganic cement with organic binders (USEPA 1985).

Treatment effectiveness

Leachability and mechanical tests performed on both the STABLEX product and the asphalt/sulfur blend indicate that these materials have a strong

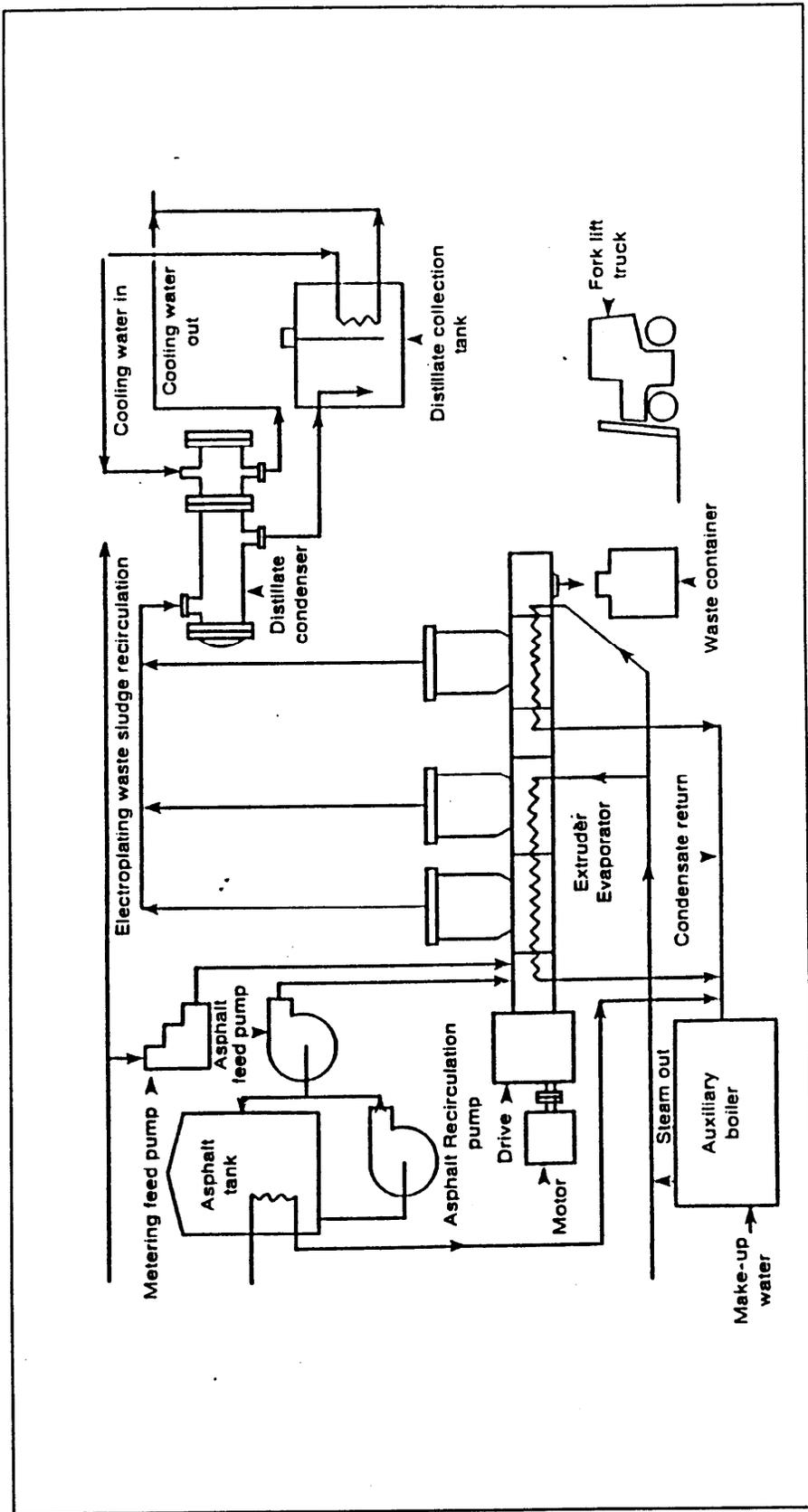


Figure 23. VRS process for microencapsulation (process flow diagram) (from Brenner and Rugg 1982)

resistance to chemical attack and can withstand mechanical stresses. (Note that the TCLP test nevertheless requires size reduction to <9.5 mm.) Metals are effectively immobilized in the additive matrix, which is dispersed through the waste. This process has been commercialized and operated at a full-scale level.

Long-term stability/performance

Both methods described previously produce very stable products. Metals are held in the additive matrix, resulting in their possible long-term immobilization; however, no long-term evaluations have been performed to date.

Residuals treatment/disposal requirements

The STABLEX product is a rocklike material. The VRS process yields a microencapsulated waste in disposal containers, which may be sent to a non-hazardous facility, depending on the regulatory climate. Emission controls on the extruder will be necessary if volatile pollutants (i.e., organic compounds) are present in the waste.

Adaptability

The process can also be used on liquid wastes and sludges. Residues from organic treatment processes may also be treated. Soils contaminated with organic wastes and metals may be treated together, but elevated processing temperatures may necessitate emission controls.

Scale up potential

Full-scale processes are presently feasible. Units with capacities of 25 tons/week and 50 tons/week have been suggested in the literature.

Potential disqualifiers

Principal concerns regarding the application of microencapsulation are listed below.

- a.* While this process requires extensive soil handling and processing at elevated temperatures, no serious disqualifiers are indicated.
- b.* If the soil were not backfilled on the original site, the stated cost would be increased by costs for backfill with imported soil and waste disposal.

Macroencapsulation

Description

This process involves encapsulation of a block of hazardous waste with a polymer such as HDPE to render it environmentally acceptable. Few experiments and pilot-scale studies have been conducted to evaluate the capability of different types of polymers to provide an acceptable and stable covering. The most detailed study to date is the one performed by TRW, Inc., for the USEPA in 1977 (TRW Systems Group 1977). This detailed study first considered the suitability of certain polymeric materials as liners. Laboratory tests were performed on 3-in. waste cubes (bound internally with a polybutadiene binder) encapsulated with a 0.25-in.-thick polyethylene jacket. This is actually a more secure combined micro- and macroencapsulation process. These tests showed that the encapsulation resulted in the retention of the contaminants in the waste, even when subjected to severe leaching conditions. Mechanical tests also showed that the encapsulated wastes were capable of withstanding substantial compressive stresses. The product of this treatment process could be disposed in a nonhazardous landfill, if delisted.

Subsequent TRW study included the development of a process design and cost estimating. Figure 24 shows the process flow diagram for a full-scale waste encapsulation process. This process would yield a 2-ft cube of waste, weighing between 600 and 1,000 lb, encapsulated by a 0.25-in. polyethylene jacket. Cost estimates indicated that treatment cost would be \$91/ton of waste (for a 20,000 ton/year throughput, 1977 cost). Fifty percent of this cost was attributed to the cost of the covering (HDPE) and binding (polybutadiene) resins. This does not include costs for excavation, backfilling, and encapsulated waste disposal. The researchers have specifically recommended this process for treating metal-contaminated wastes.

Lubowitz and Wiles (1981) reviewed three methods for encapsulating hazardous waste. The first method, the TRW process, was described earlier. The second method involves coating the fiberglass containers that hold the hazardous waste, by spraying or brushing on a covering. The third method involves overpacking of a standard 55-gal drum (which contains hazardous waste) with a welded polyethylene container (85-gal capacity). Figure 25 shows the three methods (schemes) reviewed by Lubowitz and Wiles (1981). The third method is usually applicable to liquid wastes stored in the 55-gal drums and is a means of preventing leaks from the drums. Presumably, it could be adapted to treat metal-contaminated soils. However, the costs associated with this method of disposal would be high, as wastes would have to be drummed first and subsequently overpacked. Lubowitz and Wiles (1981) estimated that it would cost \$253/ton (1980 figures), assuming that 80,000 55-gal drums are disposed per year.

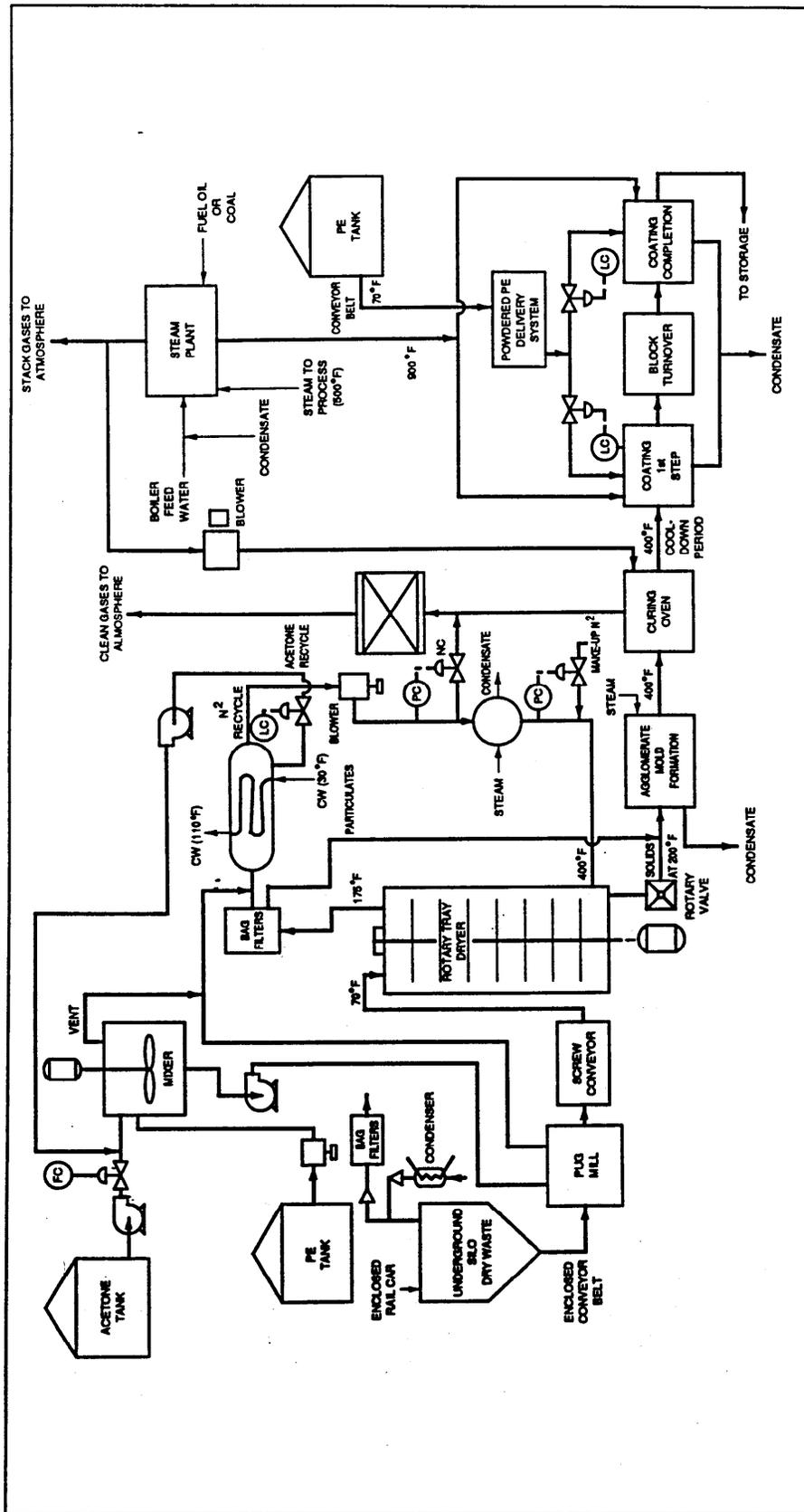


Figure 24. TRW process for macroencapsulation (process flow diagram) (after TRW Systems Group 1977)

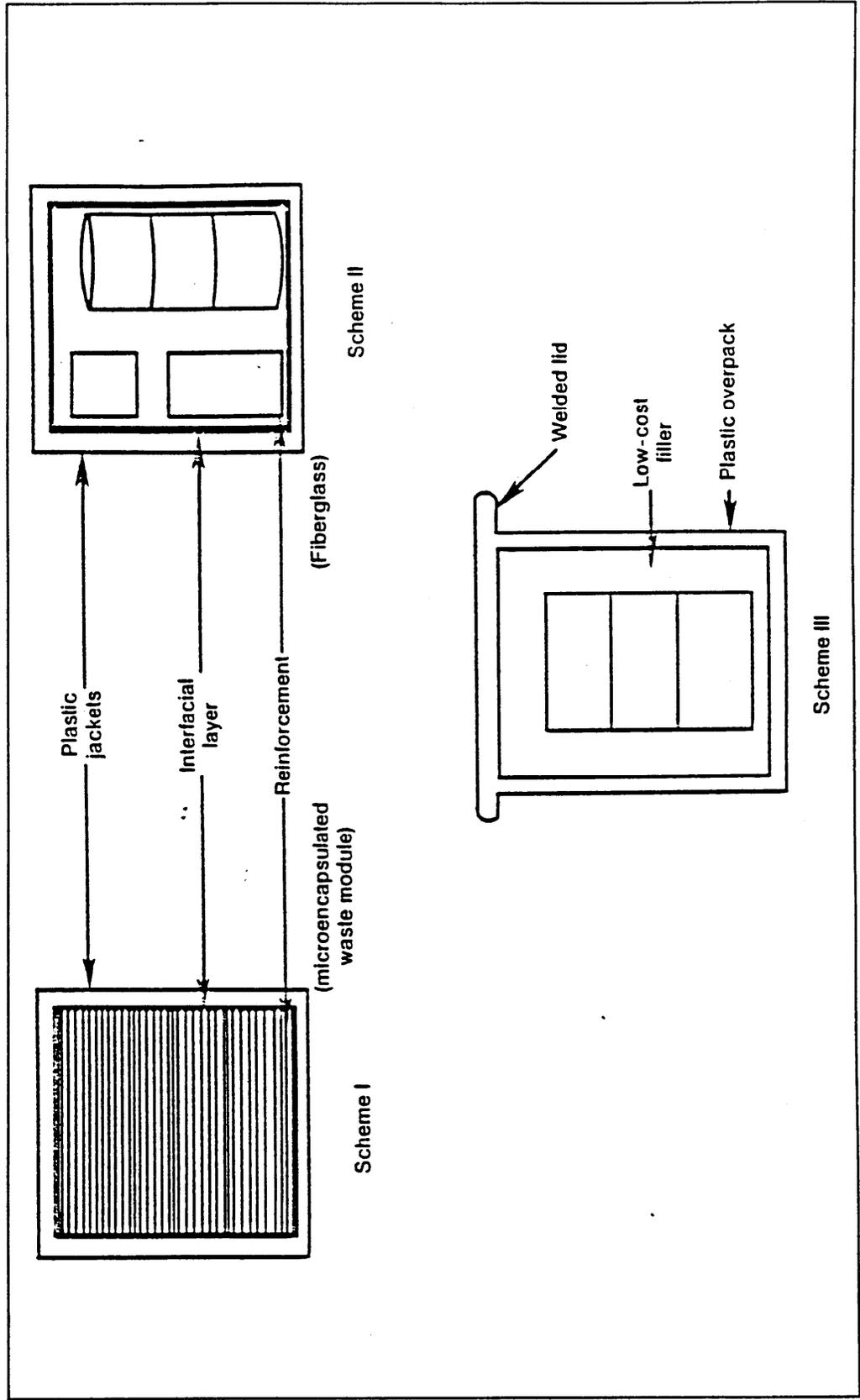


Figure 25. Method for encapsulating hazardous waste (Scheme I - resin fused onto the surface of microencapsulated waste; Scheme II - resin fused onto or sprayed fiberglass substrate holding containers of waste; Scheme III - overpacking of 55-gal waste containers with welded plastic containers)

Treatment effectiveness

Experimental data indicate that microencapsulation combined with macroencapsulation (the TRW process) is an effective means of preventing metal contaminants from leaching into the receiving waters. Coupled with this is the added advantage of forming a mechanically strong block, which allows for easy disposal in a nonhazardous landfill. Studies have shown that the final encapsulated product can contain up to 94 percent of waste by weight (Lubowitz and Wiles 1981). Macroencapsulation consisting solely of a secure outer container may have a lower effectiveness, since breach of the outer container may result in leakage. The size reduction requirement (<9.5 mm) for TCLP effectively requires the contained wastes to meet leachability standards, regardless of the "macro" container. The outer container thus becomes "added," not required, insurance.

Long-term stability/performance

Compared with chemical stabilization, macroencapsulation has a greater reliability in immobilizing metals in soils. This is because stabilization processes rely on the chemical affinity between the metal and the stabilization agent and are therefore susceptible to breakdown when soil conditions such as pH change dramatically. Encapsulation, on the other hand, can be used on a number of types of wastes, regardless of organic compound content, and encapsulated wastes can withstand severe chemical and mechanical stresses.

Residuals treatment/disposal requirements

The encapsulated waste (unconfined or drummed) will have to be disposed in a landfill. These treated wastes exhibit excellent resistance to chemical attack and leaching and may qualify for disposal in a nonsecure landfill. The wastes still face the significant hurdle of delisting. The contaminant still remains and thus the potential of leaching still exists.

Adaptability

One of the distinct advantages of this process is that it may be used to treat a wide variety of wastes. Liquids in drums would have to be stabilized with a pozzolanic material, before being overpacked with HDPE, to comply with the recent Resource Recovery and Conservation Act (RCRA) rules prohibiting disposal of liquids in landfills. The process should be applicable to soils contaminated with metals and organics. Residues from organic treatment processes may also be treated.

Scale up potential

It is anticipated that the process can be readily scaled up, although the microencapsulation/macroencapsulation version does present a difficult material-handling application.

Potential disqualifiers

Principal concerns regarding application of the macroencapsulation process are listed below.

- a. Preliminary indications are that the costs of disposal, especially when drums are overpacked with polyethylene, are high.
- b. The process may involve disposal of the encapsulated waste in a secure landfill. This is because the encapsulated waste may still be considered hazardous. Questions may be raised over long-term performance.
- c. Excavated areas would have to be backfilled with fresh soil.

Secure Landfill

Description

This method is not a "treatment" technology but is, rather, an established commercial disposal technique. It is included here as the basis for comparison of treatment technologies. In addition, some treatment technologies may clean the soil of metals by producing a waste concentrate that requires subsequent treatment or disposal. The most likely disposal option is a secure landfill.

All contaminated soils would be removed from the site using standard construction equipment--backhoes, draglines, dozers, etc. A "secure" landfill is a RCRA-permitted facility that is designed and constructed to meet all applicable Federal, state, and local laws and regulations. At a minimum, these facilities now have double liners with a leachate collection and monitoring system to detect potential leakage and groundwater contamination. Extensive USEPA regulations exist for such hazardous waste disposal facilities, to minimize harm to the environment.

Landfill liners may be constructed of chemically resistant polymeric membranes (e.g. HDPE) and/or natural low-permeability soils (clays). Another material suggested in the past as a separate liner or composite liner component is asphalt bitumen. The liner/cap system provides for surface runoff away from the fill, and for collection of any infiltration or leachate. The liner materials are designed to be resistant to chemical attack and must be carefully constructed and joined to prevent leakage. A typical double-lined landfill design is presented in Figure 26.

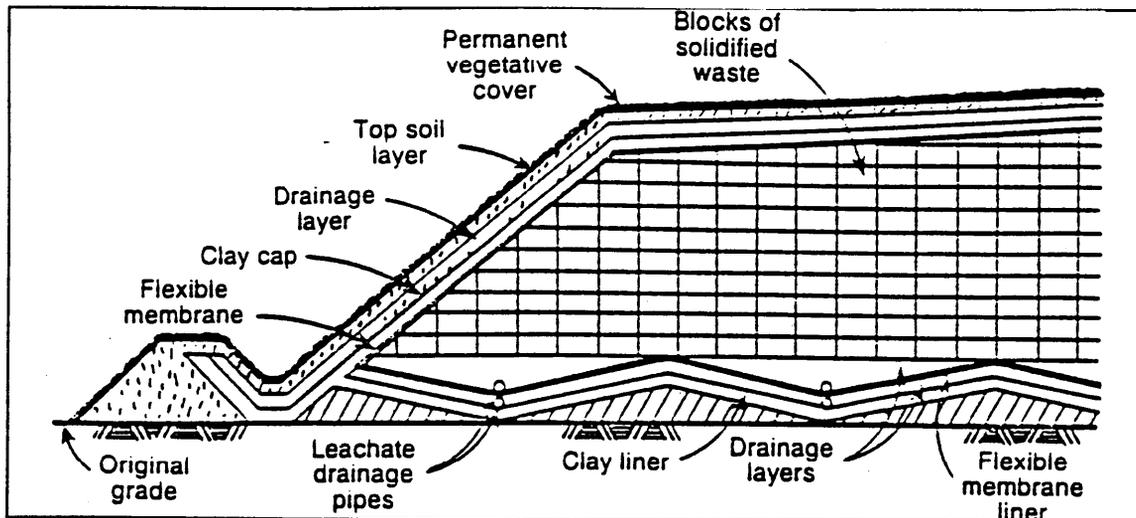


Figure 26. Cross section of secure landfill (after Weston 1987)

A secure landfill can be constructed onsite (if the volume of waste warrants) or shipped to an offsite landfill. Since dry metal-contaminated soil can be expected to be quite compatible with most liner materials, codisposal with more chemically active hazardous wastes (e.g., solvents, acids) would be undesirable.

The offsite disposal option has been used as a remedial action at many Superfund sites. In many instances, only "hot spots" (high-contamination areas) are excavated and disposed offsite. This reduces costs, as the volumes of soil/waste that must be disposed are lower. The overall cost of disposal depends on the type of waste, distance from site to landfill, volume of waste, etc. The USEPA estimated that landfilling costs are approximately \$240/ton for highly toxic wastes, \$120/ton for ignitable wastes, \$80/ton for most industrial sludges, and \$40 to \$50/ton for municipal sludges. The cost for disposal of metal-contaminated soil is expected to be in the low to middle range. However, landfill disposal costs are rising rapidly.

Treatment effectiveness

This option is an available and effective means of remedying a contamination problem. The source of contamination is removed from the site. The extent of removal, e.g., to background or to regulatory levels, is based upon an assessment of all the factors associated with the site cleanup. The disadvantage of this method is that the problem is simply transferred to another site, though a more secure one. Contaminant migration is controlled, and performance can be readily monitored.

Long-term stability/performance

A well-designed landfill may offer a safe, long-term alternative for management of contaminated soils for up to 30 years. Long-term stability and performance would depend on how the facility is operated and maintained over time. While landfill design has improved, the long-term performance with regard to natural forces (e.g., erosion and the potential for major events, such as earthquakes), chemical resistance, and physical strength may be a concern.

Residuals treatment/disposal requirements

This is not a treatment technique and does not yield any residues.

Adaptability

Landfills can accept a wide variety of wastes, including sludges, residues, and soils containing organic compounds. Again, USEPA regulations specify treatment, storage, and disposal requirements for all wastes. In addition, recent USEPA regulations restrict disposal under landban rules, and in many cases, wastes require pretreatment prior to landfilling. However, the RCRA reauthorization is likely to restrict landfilling of chlorinated organics and metals at high concentrations in the future.

Scale up potential

Secure landfilling is the most widely available commercial technology and is best suited to large-scale operation since maintenance and monitoring activities must be conducted regardless of size.

Potential disqualifiers

Principal concerns associated with the use of secure landfills are summarized below.

- a.* Limited availability of appropriate landfill capacity.
- b.* The RCRA reauthorization legislation has resulted in banning landfilling of many inorganic wastes now requiring pretreatment (such as S/S) prior to landfilling.
- c.* Liability associated with future potential contamination or environmental problems at the landfill still rests with the generator.
- d.* Indefinite monitoring would be necessary to ensure continued good performance. Future leakage could require remedial action.

Geologic Isolation

Description

Geologic isolation is a disposal method and not, strictly speaking, a waste "treatment" technology. This method involves excavation of the contaminated soil, drumming it, and placement (of the drums) in secure, stable geologic formations, which results in isolation of the waste from the surrounding environment.

One proposed application of this technique is radioactive waste disposal in deep salt mines. This has been studied by the U.S. Department of Energy (DOE) for disposal of high-level radioactive waste.

Another "more permanent" option for disposal is placement in the bed of the ocean (Bove et al. 1983). Drums containing wastes are placed in stable locations that contain unconsolidated clay beds. The drums would be placed well below the sea and would be covered by the clay upon placement. In addition to the stability of the beds, clay has sorptive properties that would enable minor leaks to be absorbed by the bed materials. The lack of oxygen is known to prevent oxidation and biodegradation. This method is being used by European countries for disposing low-level radioactive wastes and has been studied by the DOE.

Ocean disposal of hazardous waste is viewed with increased disfavor by the many countries. Apart from degradation of the ocean beds by disposal, additional uncertainty exists regarding the long-term effects of this process. Accordingly, the United States has banned ocean disposal of hazardous waste.

While low-level radioactive wastes are expected to become nonhazardous in 10 to 100 years, metals will retain their hazardous properties indefinitely. Since seabed stability is difficult to predict, the long-term security of this approach may also be in doubt.

The cost for this technology is expected to be quite high, because of the problems of accessibility and disposal site development, in addition to the costs for excavation, transportation, and backfilling.

Soils with low metal concentrations and low leachability could potentially be disposed directly onto the ocean with little adverse effect at a significantly lower cost. This would likely encounter serious regulatory and institutional obstacles and is, therefore, considered infeasible.

Treatment effectiveness

This technology results in the removal of contaminants from the site and is therefore an effective means of remediating a metals-contaminated site. The

ability of salt domes to isolate material from the environment has been studied. Storage of petroleum gases and liquids in salt domes has been reported, and some well-known incidents of leakage have occurred. Storage of solids may be more successful, but careful site selection and development is clearly needed.

Seabed disposal has been used successfully for low-level radioactive waste disposal in Europe. Accidental release or improper placement during disposal operations may be more likely in deep sea operations, however.

Long-term stability/performance

The long-term effects of disposing sludge into the ocean appear to be deleterious. However, disposal of waste well below the seabed in stable clay sediments may provide long-term, secure storage/disposal. The ability to predict the duration of stability in deep seabeds is uncertain at this time.

Geologic isolation of radioactive wastes in deep salt mines appears to be a stable long-term disposal option. Although leakage has occurred on certain installations used for oil and gas storage, properly selected sites may provide indefinite secure disposal for solids.

Residual treatment/disposal requirements

This is not a "treatment" technique and does not yield any residues. The contaminated soil itself is disposed.

Adaptability

This method of disposal can be applied to a variety of wastes. Sludges and liquid wastes can be drummed and disposed. Wastes containing organics or residues from organic treatment processes can also be disposed.

Scale up potential

Disposal rates may be adjusted upward based on the design of mine accessways for salt mine disposal. Deep sea excavating and material-handling equipment may be increased in size and/or operated in parallel. Specific limitations on the disposal rate are not available.

Potential disqualifiers

Principal concerns regarding the application of geologic isolation are listed below.

- a. Ocean disposal might not be an available option because it may be legally or institutionally unacceptable.
- b. A few salt dome burial sites are under active consideration for radioactive waste disposal. This method may be excessively expensive for disposal of soils with very low metal contaminant concentrations.
- c. While this technology may become available commercially or under the U.S. DOE program as a more secure disposal option, it does not constitute waste treatment.

Deep Well Injection

Description

Chemical manufacturing, for instance, electroplating, produces solutions laden with heavy metals. Likewise, a number of soil remediation technologies produce residual aqueous streams contaminated with heavy metals. One approach to the disposal of these streams is deep well injection. This method involves pumping liquid wastes into porous geological formations. Done properly, this method isolates hazardous materials from the biosphere. Injection has been successfully practiced for disposal of liquid wastes, "especially when wastes are malodorous or toxic and contain little or no suspended matter" (Nemerow 1978). Use has accordingly grown as disposal to surface waters has become more restricted. The number of hazardous waste wells has increased from 30 in 1964 to 280 in 1973. By 1991, over 180 wells were in use for the disposal of dilute aqueous hazardous waste.¹ This does not include the more than 100,000 oilfield wells for return of extracted brine (Freeze and Cherry 1979). Deep well injection "has been successfully applied for disposal of organic and inorganic solutions from chemical, pharmaceutical, petrochemical, paper, and refining" (Nemerow 1978). In a more recent example, an ammonia liquor contaminated with selenium has been injected (*Federal Register* 1990).

Environmental protection requires injection of wastes into a formation that will prevent the movement of the contaminant to the surface or into drinking water supplies. Generally, the wastes are pumped into formations of porous limestone, sandstone, and dolomite capped with impermeable layers of rock such as shale. Most wells are between 300 and 2,000 m in depth and operate at flows of 500 to 1,400 L/min (Freeze and Cherry 1979). The effect of an injection well on the hydrodynamic conditions in a hypothetical horizon aquifer in which there is a regional flow is shown in Figure 27. "The injection well causes a mound in the potentiometric surface. The mound extends unsymmetrically in the direction of regional flow in the aquifer. As injection

¹ Personal Communication, 1986 (May), Bill Bonner, Battelle Pacific Northwest Laboratories, Richland, WA.

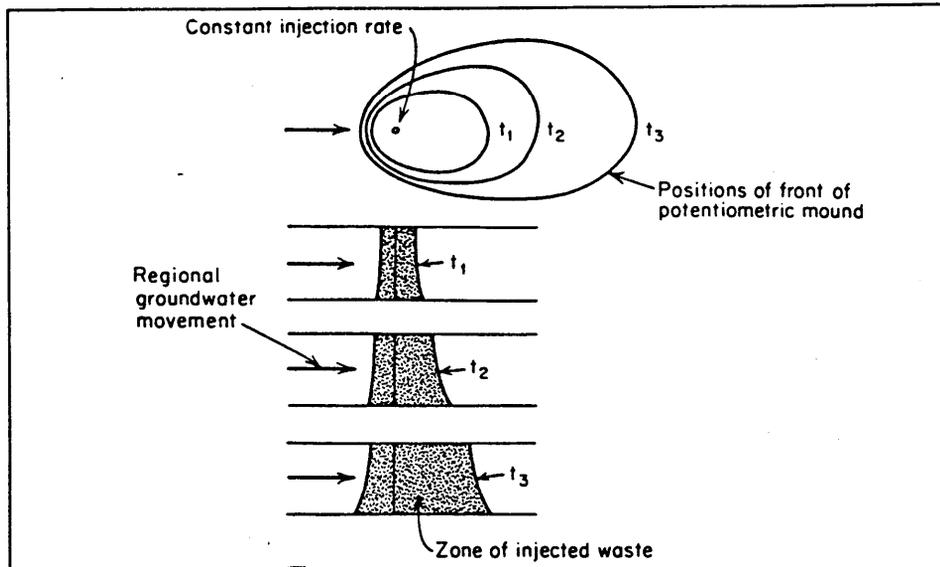


Figure 27. Potentiometric mound caused by waste disposal well and expansion of zone occupied by waste (positions at times t_1 , t_2 , and t_3) (after Kazmann 1974)

continues the areal extent of the mound spreads to occupy an ever-increasing area. The process can be viewed as the inverse of the effect of a pumping well in a confined aquifer..." (Freeze and Cherry 1979).

Factors affecting successful application of injection include geology, well depth and diameter, injection pressure, volume and rate of liquid, and characteristics of the waste.

Concern for protecting drinking water supplies (Cantger and Knox 1985, Driscoll 1986) led to the Drinking Water Act of 1974. Further requirements were formulated under RCRA and the Hazardous and Solid Waste Amendments (HSWA) of 1984. Under the most recent standards of RCRA with HSWA (*Federal Register* 1990), hazardous waste can be disposed only in a "Class I" (more specifically "IH") type well. Class I wells are those used to inject waste below the lowermost formation containing drinking water within 0.25 mile of the well bore. These wells are most frequently used for municipal and industrial injection disposal systems. Classes II-V apply to disposal of oilfield brines, injection of fluids for minerals extraction, and return of air-conditioning water, among other uses.

According to the RCRA/HSWA rules, "hazardous waste can only be injected under two circumstances: (1) when the waste has been treated in accordance with...40CFR part 268...; or (2) when the owner/operator has demonstrated that there will be no migration of hazardous constituents from the injection zone for as long as the waste remains hazardous. Applicants seeking an exemption from the ban must demonstrate either (a) that the waste undergoes a chemical transformation so as to no longer pose a threat to human

health and the environment; or (b) that fluid flow is such that injected fluids would not migrate vertically upward out of the injection zone or to a point of discharge in a period of 10,000 years use by mathematical models" (*Federal Register* 1990). Between 1985 and 1990, these more stringent regulations contributed to a decline in the number of Class IH facilities (from 95 to 51) and in the injection rate (from 11.5 to 9 billion gallons/year) (USEPA 1991).

Good engineering practice and regulation require a number of stages in the planning and construction of a Class I injection well. These include the following: (a) a thorough survey of the geology to ensure no faults or earthquake risks; (b) core sampling and determination of permeability and geochemical compatibility of the formation and the waste fluid;¹ (c) drill-stem tests to measure initial static pressure, formation permeability, and skin effect; (d) short-term pumping and injection tests; and (e) use of concentric bore holes with packing between the casings and bore hole. This prevents fluid flow from and into the formation to effectively seal all contamination in the formation. Details are shown in Figures 28 and 29.

Treatment effectiveness

This method does not represent treatment, other than that required to make the fluid compatible with the formation. As noted above, this method has been widely and successfully used for over 25 years.

Long-term stability/performance

Instances of disposal system failure and contamination of surface and near-surface waters are rare (Nemerow 1978). However, some instances have been reported, and the number may increase with the time over which strata have been used for receiving wastes (Wentz 1989). Storage in a formation will be particularly vulnerable where unplugged wells may provide pathways for waste to migrate through capping formations. The waste might then migrate to underground or even surface waters. Finally, injection is not permanent disposal. "It detains in storage and makes intractable the storage of wastes in formations that are limited in some areas and exhaustible in most areas" (Wentz 1989).

Residual treatment/disposal requirements

All significant fluid flows are injected, so few or no additional disposal requirements exist. However, pretreatment may require settling or filtering of

¹ Waste fluid reactivity or plugging with sample cores may require pH adjustment or settling and filtration.

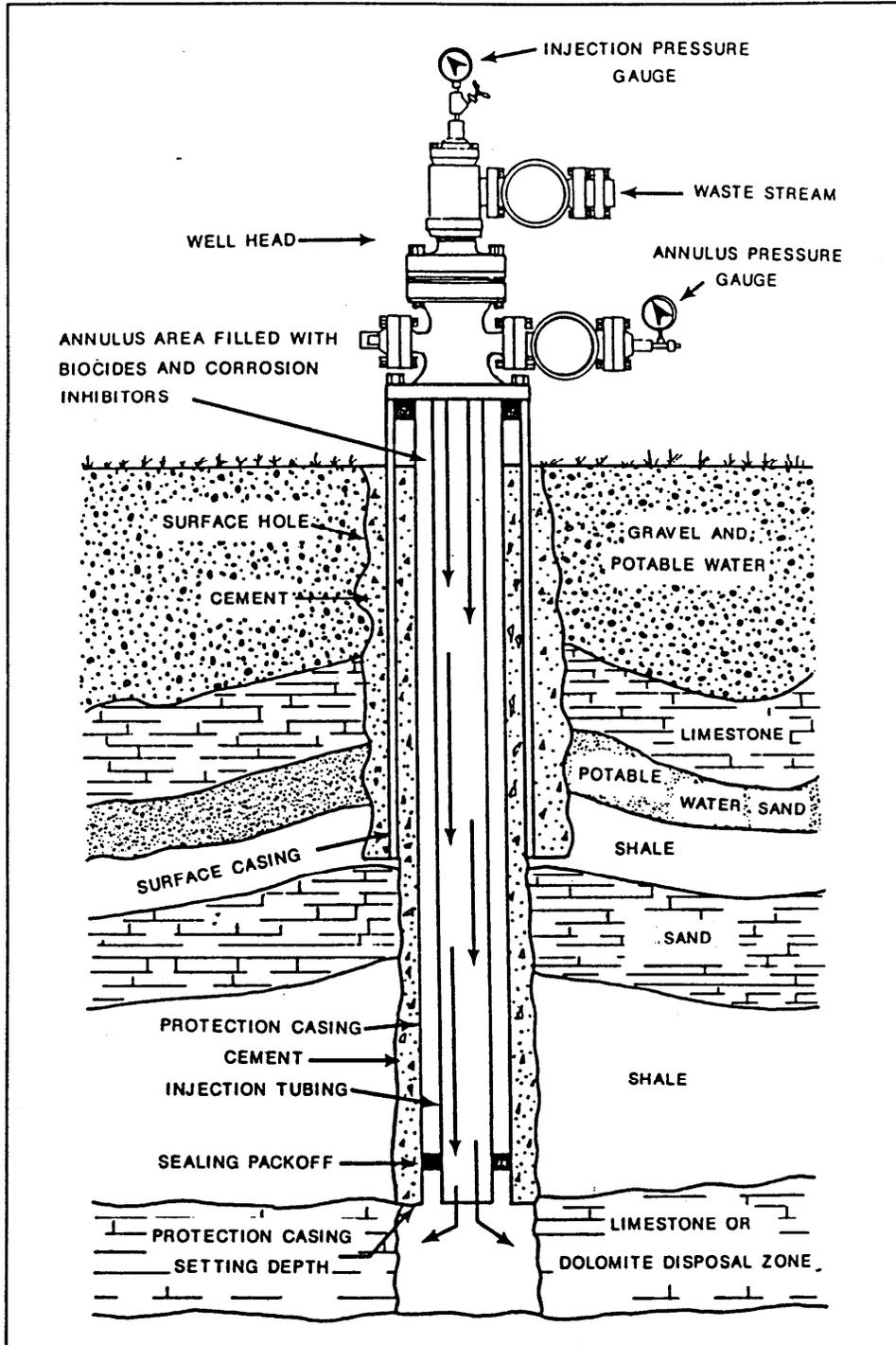


Figure 28. Design of hazardous waste disposal well (after Wentz 1989)

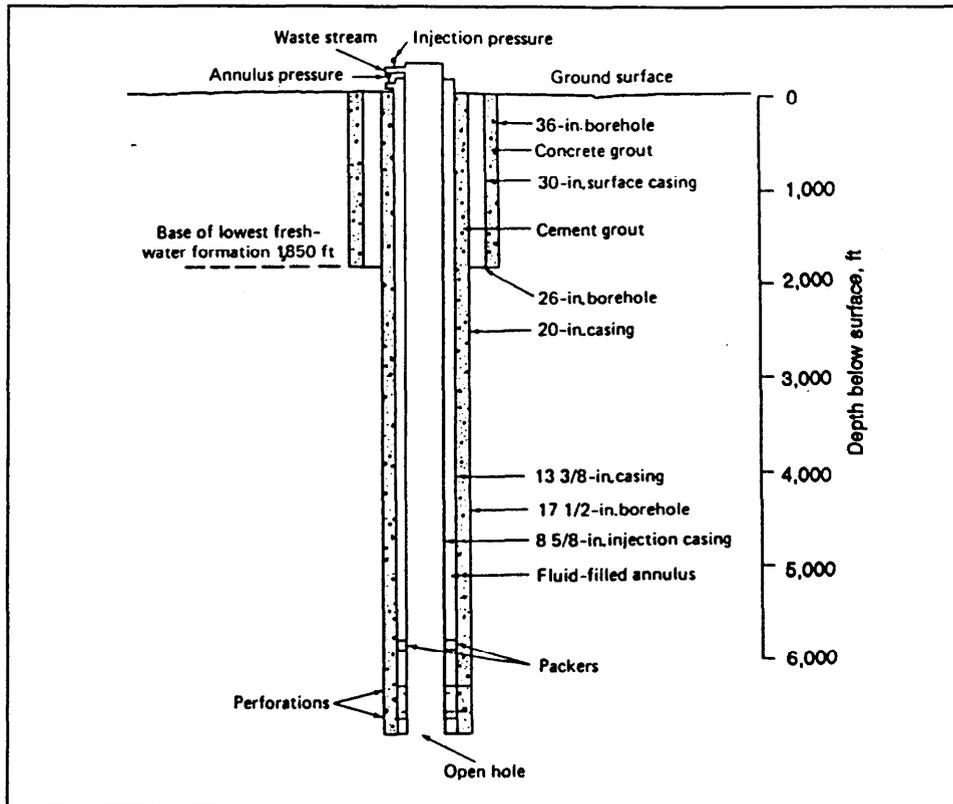


Figure 29. Injection well dimensions (case study) (after Wentz 1989)

solids before fluid injection. Any hazardous solids will have to be disposed accordingly.

Adaptability

Injection has been widely applied to disposal of organics and inorganics. However, it does have limitations for cases in which the waste reacts or plugs in the formation. Of course, the major prerequisite is that there be a suitable formation under or near the facility generating the waste.

Scale up potential

The method has been fully scaled up and successfully operated for over 25 years. All methods and regulatory requirements are in place. Costs will vary with the type of formation and pretreatment required. One set of estimates for well costs alone, for two cases, gives \$1.03 million (4,180 ft) and \$1.206 million (5,900 ft) (Wentz 1989).

Potential disqualifiers

Principal concerns regarding the use of deep well injection are as follows:

- a.* Injection will not be an option unless an appropriate formation, meeting all requirements, exists under or near the waste generator.
- b.* Limitations also result if the waste reacts with or plugs in the formation and no effective/economical pretreatment can resolve the problem.
- c.* Finally, concerns over long-term stability remain, especially when unplugged wells in one area may compromise the integrity of the capping formation, allowing waste to spread more widely.

5 Vegetative Uptake

Background

The use of plants that selectively absorb metals from soil and concentrate them in the plant biomass has been suggested as a means of removing metals from contaminated soils. The idea would involve growing specific plants on a metals-contaminated site and harvesting the plants at the end of the growing season. The harvested plants must then be disposed in an appropriate manner (e.g., incineration) (Bove et al. 1983).

The natural phenomenon of metal uptake by plants is dependent on a number of factors such as plant species, soil chemistry and types, and metal species. Generally, metal uptake is higher in acidic soils because of the higher solubility of most metal species at low pH. The soluble metal ions must then move to the roots by movement of soil moisture or diffusion, or the root will move by growing through the soil. Cation adsorption is highest at pH 5 to 7, and anion adsorption is best under pH 6 (Harward, Doyle, and Kitchens 1980; Bove et al. 1983). Differences in metal uptake between plants depend on nutrient requirements and typical growth conditions. Many plants concentrate metals only in the roots, indicating that the root surface ion exchange and/or membrane surface characteristics may present a barrier to metal adsorption into the plant tissue. Other plants that typically grow in high-mineral content soils tolerate high metal uptake by the storage of metals (complexing them with natural ligands) (Bove et al. 1983). Studies indicate widely varying properties based on the soil matrix and plant species.

Extensive research has been conducted on the uptake of metals from natural soils, urban soils, and sewage- and sludge-amended soils (Keeling et al. 1977; Brown 1978; Brown, Thomas, and Slowey 1983; Jones and Thornton 1983). Research on aquatic plant uptake of metals has also been conducted (Wolverton 1975; Wolverton and McDonald 1975a, b).

Much of the work conducted on soils was directed at public health impacts due to metals uptake to food crops. This has shown that metals levels are often increased, but not to toxic levels. If metals concentrations are too high, toxicity can result. These studies do not indicate high rates of metal uptake,

however, with one study citing 1 to 2 percent uptake of Cd, Cu, Pb, Ni, and Zn in Bermuda grass (Brown, Thomas, and Slowey 1983).

Waterhyacinth and alligator weed have been fairly effective in removal of soluble trace metals (Cd, Ni, Pb, Hg, Co, Zn) from water. Dry weight plant metal concentrations were below 1 mg/g (1,000 ppm) for individual metals. Water concentrations were reduced to detection limits of 1 ppb (Wolverton 1975; Wolverton and McDonald 1975a,b).

Little study in vegetative uptake has been directed toward the objective of maximizing the removal of heavy metals from soil. If plants that perform effectively can be identified, they can be harvested and disposed. Because of phytotoxic effects on plant growth, applications may be limited to lower metal concentrations. Plant uptake may result in concentration of metals, but this is limited in biological systems. This results in a significant residual vegetation volume that will require further management. Disposal in a hazardous waste landfill is an option for this residue. Alternatively, drying and incineration can result in significant volume reduction, but metals will remain in the ash or off-gas dust, requiring treatment or disposal as a hazardous waste. RCRA definitions of hazardous waste incineration residue as hazardous may limit options.

Description

Treatment effectiveness

Although much work has been published on vegetative uptake, as described above, few studies have been directed toward cleanup of metal-contaminated soils. The study by Brown, Thomas, and Slowey (1983) indicated that only 1 to 2 percent of metals in the soil can be removed by Bermuda grass.

Harward, Doyle, and Kitchens (1980) conducted a detailed study on the feasibility of using vegetative uptake as a means of cleaning a site contaminated with radionuclides. They calculated that the time required for cleaning up a hypothetical site of 1 acre contaminated to a depth of 6 in. would be unreasonably long (6.7×10^5 years). Therefore, they concluded that this method was infeasible for the radionuclides investigated (plutonium, uranium, thorium, and radium).

Any treatment achieved would necessarily be limited to the active plant root zone. Based on the limited information available, it appears that the time involved in cleanup of a site using this "process" would be very great. In addition, significant concentration of metals may not be achievable by plant uptake alone. Additional treatment (i.e., incineration) is necessary. Therefore, this method is not likely to be an effective means of removing metals from soils.

Long-term stability/performance

Once removed, of course, the site will remain free of metal. From a long-term perspective, this method may be considered ineffective because of the very slow rate of metals removal. During an extended cleanup, the metals may migrate offsite or away from the root zone before recovery is achieved.

Residuals treatment/disposal requirements

The harvested vegetative matter containing metals will require disposal. If directly landfilled, a large volume must be managed. If dried and incinerated, off-gas dust collection may be necessary, and ash and dust residuals containing metals will require disposal.

Adaptability

Removal of organic compounds with aquatic plants has been shown to be effective for low concentrations. Performance by plants selected for their ability to absorb metals remains a subject for future study. Vegetative uptake could be applied to residues where soil properties have been maintained sufficiently to support plant growth. Incineration residue is unlikely to meet these requirements, but other nondestructive soil treatment residues could be treated.

Scale up potential

This technology could readily be applied to large land surface areas utilizing normal agricultural techniques. It is limited to treatment of the soil root zone, however.

Potential disqualifiers

Principal concerns with regard to the application of vegetative uptake are as follows:

- a.* Very slow removal rates for certain metals render the process ineffective.
- b.* Extensive long-term site management requirements, including harvesting of crops.
- c.* Harvested crop/vegetative matter has to be disposed.
- d.* Poor transport of metals to root zone.

- e. If metals *are* sufficiently mobilized to move toward the root zone, they may also be mobilized toward aquifers.

6 Summary and Conclusions

Technologies for the treatment of heavy metals-contaminated soil have been critically reviewed, and the results are presented in this report. The scope of this review includes a survey of metals contamination at Army installations, a review of regulatory standards, and a review and assessment of 24 technologies.

This report reviewed and assessed the technologies without ranking. A separate report will integrate site survey and regulatory review to prioritized technologies. This discussion grouped the processes into four categories: physical and chemical; thermal; immobilization, stabilization, and disposal; and vegetative uptake. Each technology was described and assessed according to treatment effectiveness, long-term stability/performance, residuals treatment/disposal requirements, adaptability, scale up potential, and potential disqualifiers.

The major conclusions from this review are:

- a. Currently, few advanced technologies are widely practiced for heavy metal-contaminated soil.
- b. The most common "treatments" are dig-and-haul (to a landfill) and solidification/stabilization.
- c. A number of the technologies reviewed offer promising performance for a variety of applications.
- d. Questions or uncertainties exist for many of these technologies. Two major concerns are production of residual streams and long-term stability of treated metals left in the soil.
- e. Additional research and development is needed to better understand the fundamentals of some processes and to resolve uncertainties for others.

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13. ABSTRACT (Maximum 200 words) Past military and industrial activities have contaminated numerous U.S. Army installations with metals, solvents, and explosives. The Army's Installation Restoration Research Program (IRRP) seeks to clean up contaminated soils and groundwater that could adversely impact the environment and restrict the use of Army land. Early studies revealed an immense scope of needed restoration and many contaminants unique to the Army. In response, the Army initiated research to develop more effective, economical, and environmentally responsible technologies for treating contaminated soils. This report reviews treatment technologies for heavy metal-contaminated soil for development and use at U.S. Army installations. Assessment criteria included treatment effectiveness, long-term stability/performance, residuals treatment/disposal requirements, adaptability, scale up potential, and potential disqualifiers. Where available, cost estimates are given. The technologies are grouped in four categories: physical/chemical, thermal, immobilization/stabilization/disposal processes, and vegetative uptake. Results show that only two methods are widely practiced: dig-and-haul and immobilization/ stabilization. While effective in the near term, costs associated with these approaches are increasing. Also, these approaches carry long-term liabilities, <p style="text-align: right;">(Continued)</p>				
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consume secure landfill space, and may not satisfy future regulation. A number of promising technologies are available that could be developed within a 5-year time frame. However, questions and uncertainties exist for a number of them. Appropriate research and development should be directed at the most promising technologies.

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Contaminated soils
Heavy metals
Metals cleanup
Metals contamination

Soils
Treatment
Treatment technologies