CONF-930205--25

Soil Washing as a Potential Remediation Technology for Contaminated DOE Sites*

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ANL/CMT/CP--78935

DE93 009205

For presentation at
Waste Management '93
Tucson, Arizona
February 28 - March 4, 1993

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*Work supported by the U.S. Department of Energy, Office of Technology Development under Contract W-31-109-ENG-38.

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ABSTRACT

Frequently detected contaminants at U.S. Department of Energy (DOE) sites include radionuclides, heavy metals, and chlorinated hydrocarbons. Remediation of these sites requires application of several technologies used in concert with each other, because no single technology is universally applicable. Special situations, such as mixed waste, generally require innovative technology development. This paper, however, focuses on contaminated soils, for which soil washing and vitrification technologies appear to have wide ranging application potential. Because the volumes of contaminated soils around the DOE complex are so large, soil washing can offer a potentially inexpensive way to effect remediation or to attain waste volume reduction. As costs for disposal of low-level and mixed wastes continue to rise, it is likely that volume-reduction techniques and in-situ containment techniques will become increasingly important. This paper reviews the status of the soil washing technology, examines the systems that are currently available, and discusses the potential application of this technology to some DOE sites, with a focus on radionuclide contamination and, primarily, uranium-contaminated soils.

INTRODUCTION

Until about a decade ago, soil washing was primarily tried as a technique for recovering gasoline from contaminated soils. Recent interest in the technology as a remediation tool has led to a number of developments and processes for sites contaminated with many different types of contaminants.

In conventional applications, the soil washing process extracts contaminants from a sludge-soil matrix by using a liquid medium as the washing solution. This washing solution is then treated for removal of the contaminants via a conventional wastewater treatment system. Soil washing can be used on sludge and excavated soils fed into a contactor or washing unit. A similar process, known as soil flushing, can be applied in situ by using an injection/recirculation system for shallow contamination. Washing fluids may be composed of water, organic solvents, water/chelating agents, water/surfactants, and acids or bases. After the

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contaminants have been removed from the washing fluid, the fluid can be recycled through the soil washing unit. In the case of in-situ soil flushing, the treated washing solution can be reinjected into the soil via a recirculation system. Soils may require multiple washing/flushing cycles for effective contaminant removal. Only certain types of soils can be washed frequently, gas determined by the uniformity of the soil.

Depending on the type of washing fluid additives used for enhancement of contaminant removal, waste types that can be removed by using soil washing/flushing include: heavy metals (e.g., lead, uranium, copper, zinc), halogenated solvents (e.g., TCE, trichloroethane), aromatics (e.g., benzene, toluene, cresol, phenol), gasoline and fuel oils, PCBs, and chlorinated phenols.

Radionuclides, heavy metals, and chlorinated hydrocarbons are the most frequently detected contaminants at DOE sites. Because the volumes of contaminated soils around the DOE complex are very large, soil washing can offer a potentially inexpensive technique to effect remediation or to attain waste volume reduction. This technique is of interest to DOE, and it is part of an integrated demonstration at the Fernald site, where technologies for remediating uranium-contaminated soils are being demonstrated.

A number of companies are now marketing their versions of the technology. These companies include Biotrol; Westinghouse; AWC Inc.; TechTran, Inc.; and Bergmann, USA. In addition, the technology has been applied overseas -- most prominently in the Netherlands.

The technology of soil washing is, however, very site-specific and contaminant-specific. Highly variable soil conditions can lead to inconsistent results, and higher percentages of silt or clay can lead to solid/liquid separation problems (characteristics around the DOE complex vary greatly -- ranging from high clay/silty soils at the Oak Ridge Reservation to silty sand at Hanford). An understanding of the fixation mechanisms through which contaminants are held onto the soil particles is also important. While soil washing does not reduce toxicity, it does provide a means of reducing the volume of contaminated material. It is clear, however, that remediation of some contaminants at DOE sites may be amenable to soil washing. In this study, we review the status of the technology to date, as well as the contaminant and soil characteristics at several DOE sites, with an objective to match the potential application of these processes to these sites.

The literature survey includes published reports and papers; information from national laboratories; searches of the Argonne Information Management System (AIMS), ENERGY, and NTIS databases; and vendor information from the U.S. Environmental Protection Agency's (EPA's) VISITT database (1). This paper presents the results of our analysis.

TYPES OF CONTAMINATION

Contaminants at DOE waste sites include radioactive, hazardous, and commingled materials and waste. Among the most frequently reported types of contaminants in soils and sediments, as well as in groundwater, are chlorinated hydrocarbons, radionuclides, and metals (2).

Because of their volume, uranium-contaminated soils present one of the major cleanup challenges to DOE.

The DOE waste sites include facilities operated by DOE, along with non-DOE sites that DOE, as successor to the Manhattan Engineer District (MED) and the Atomic Energy Commission (AEC) is responsible for cleaning up (i.e., sites that performed uranium mining and processing, as well as other defense-related research and activities). Ninety-one waste sites at 18 major DOE facilities geographically distributed across the country were recently surveyed to determine the presence of various types of contaminants (2). The facilities in the survey included Fernald Feed Materials Production Center, Hanford Site, Idaho National Engineering Laboratory, Kansas City Plant, Lawrence Livermore National Laboratory, Los Alamos National Laboratory, Mound, Nevada Test Site, Oak Ridge Reservation, Pantex Plant, Pinellas Plant, Portsmouth Gaseous Diffusion Plant, Rocky Flats Plant, Sandia National Laboratory, Sandia National Laboratory (Livermore), Savannah River Site, Argonne National Laboratory, and Brookhaven National Laboratory.

The contaminants at these sites include metals such as lead, chromium, mercury, arsenic, zinc, copper, cadmium, barium, and nickel; radionuclides such as uranium, radium, thorium, plutonium, cesium, tritium, strontium, cobalt, technetium, and iodine; chlorinated hydrocarbons such as trichloroethylene, 1,1,1-trichloroethane, 1,2-dichloroethylene, tetrachloroethylene, 1,1-dicholroethane, chloroform, carbon tetrachloride, and chlorobenzene. Additionally, the contaminants present at some of the sites include pesticides, explosives, complexing agents, organic acids, PCBs, and fuel hydrocarbons.

Frequently, these contaminants are present or were even disposed of as mixtures. The survey data have shown that radionuclides, heavy metals, and chlorinated hydrocarbons (in that order) are the three most frequently detected contaminants in the soils and sediments of the 91 waste sites (2). In groundwater, the most frequently detected contaminants are chlorinated hydrocarbons, radionuclides, and heavy metals (in that order). Uranium, which is the most frequently observed of the radionuclides, is also found in the groundwater at DOE sites at a frequency almost equal to that of tritium. Uranium-contaminated soils exist at Fernald, Hanford Site, Oak Ridge Reservation, Rocky Flats Plant, and Savannah River Site. Uranium is often present in conjunction with other categories of contaminants such as metals, organic acids, complexing agents, or ketones. Their presence can produce effects that can change the solubility and mobility of the uranium waste and affect the performance of the remediation technologies.

SOIL CHARACTERISTICS

An aspect of a contaminated site that is often equally as important as the type of contamination is the matrix where the contamination is found. Soil matrix (pH, cation exchange capacity, and co-contaminants) affects the pollutant adsorptive behavior. The effectiveness of a remediation technology on contaminated soil may depend on the composition of the soil. Therefore, it is important to look at the primary properties of various components of soil.

The DOE sites cover different types of geologic, hydrogeologic, and climatic terrains that range from humid and clayey sites, such as the Savannah River Site in the southeast, to arid and sandy sites, such as Hanford Site in the northwest. Descriptions of the soil and hydrogeological characteristics of a few major DOE sites considered in this paper are briefly described here.

Oak Ridge Reservation. Silty clay with chert fragments over fractured bedrock; unconsolidated zone of 0.4-1.7 m; hydraulic conductivity of $<10^{-5}$ cm/s.

Rocky Flats Plant. Nederland cobbly, gravelly sandy loam: deep, well-drained soil on high terraces; side slopes and alluvial fans; surface layer of cobbly sandy loam about 10 cm thick; subsoil of cobbly sandy loam 15-30 cm thick; moderate permeability; effective rooting depth of $\geq$1.5 m; moderate available water capacity; slow surface runoff; slight erosion hazard.

Denver-Kutch-Midway soils: strong/moderately steep soils on upland ridges and valley slopes bordering drainage ways; well-drained surface layers of ~13 cm; moderate to low permeability; effective rooting depths of 0.2 m to 1.5 m; high, moderate, and low available water capacity; high water erosion hazard.

Hanford Site. Silt, silty sand, coarse/medium sand, and gravel; surface: light-brown, slightly silty fine sand, deposited by the wind; 0.3 m to >4 m deep: 69-97% sand, 1-26% silt, 1-5% clay; on site E of 200 area: 7-53% sand, 32-75% silt, 5-19% clay; below-Pasco gravels (Hanford formation): silty sandy gravel - 50% gravel, 40% sand, 10% silt. Thickness of 6 m to some 100 m or more. Below this, but too deep to excavate, is the Ringold formation.

Savannah River Site. Bimodal, containing quartz sand and kaolin clay; clay content varies between 10-50% by volume.

Fernald. Fincastle soils, consisting of silty loam in the upper 20 cm and silty clay loam down to 0.3-1.5 m, underlaid by a 0.3-15 m layer of glacial overburden consisting largely of yellowish to grayish-brown silty clay with some gravel lenses of silty sand, and then underlaid by a 27-55 m layer of glacial outwash -- sand and gravel that contain the Great Miami Aquifer. In much of the production area, where the soil has been disturbed, the original soil is often mixed with gravel, and soil layers in the upper few feet have often been somewhat mixed and homogenized.

BRIEF REVIEW OF REMEDIATION TECHNOLOGIES

In screening the literature, it was noted that treatment technologies could be grouped into three broad categories on the basis of the approach taken toward treating the waste; namely, containment (in place), in-situ remediation, and retrieval and treatment. A number of technologies fall under each category. Containment includes protective barriers, grouting, vitrified barriers, biological immobilization, deep soil mixing, and cryogenic confinement; in-situ treatment includes in-situ vitrification, electrokinetics, in-situ bioremediation, biodenitrification, radio frequency heating, in-situ heating, soil-gas extraction, fluidized zeolite bed, and chemical oxidation; retrieval and treatment includes soil washing, bioremediation, robotics for buried objects, robotics for sludges and sediments, incineration, photon processes, supercritical water oxidation, autoclaving, gamma irradiation, closed loop sluicing, pneumatic pickup, and ex-situ vitrification.

To be useful for dealing with radionuclides, technologies must provide isolation or long-term immobilization of radioactive constituents or their removal for treatment, reduction or elimination of chemical toxicity, minimization of environmental impacts to the surrounding environment, and application at an affordable cost. Restricting the general list to specific uranium-applicable technologies that have been developed to at least a pilot scale stage results in a shorter list of applicable technologies for uranium-contaminated soils:

1. Disposal and Containment. Capping, vertical barriers - slurry walls and grout curtains, land encapsulation, land spreading, underground mine disposal, and ocean disposal.

2. Remediation - In Situ. In-situ vitrification, in-situ solidification/stabilization, soil flushing, electrokinetics, and in-situ bioremediation.

3. Remediation - Ex Situ. Soil washing, bioremediation, other vitrification technologies, and solidification/stabilization.

Other specific emerging technologies include in-situ aqueous biphasic extraction for actinide recovery from solid wastes, combined physical and biochemical treatment of contaminated soils, soil washing for mixed wastes, and in-situ chemical immobilization.

Although most DOE sites do not come under the direct jurisdiction of the EPA, some sites have been designated as Superfund or other special sites and thus are affected by the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA). In addition, site cleanups must also comply with Applicable, Relevant and Appropriate Requirements (ARAR's). In general, to be easily available for future site clean up, technologies must fulfill the requirements of currently enforced legislation, as well as try to anticipate legislative trends. The final waste form must also pass EPA's toxicity characteristics leaching procedure (TCLP) test. By itself, soil washing may rarely satisfy such requirements; instead, it provides a waste volume reduction technique as the front end of a technology train. In some cases -- certain radionuclides, for example -- it may be possible to use soil washing to meet the residual levels for clean soil.

SOIL WASHING AND ASSOCIATED TECHNOLOGIES AND THEIR APPLICABILITY TO DOE SOILS

Soil washing generally involves water (with or without additives) to wash contaminated waste. Some contaminants are soluble in water, while others are washed free of the soil particles. Physical separation techniques are then used to separate the soil into clean and contaminated fractions. These techniques include screening, classification, flotation, and gravity concentration to separate fine soil particles that may contain radioactive contaminants. Screening is mechanical separation based on particle size differences. Classification involves the separation of particles based on their settling rate in fluids -- normally water.

Soil washing, as generally applied, involves in-tank treatment of excavated soils and is normally successful for soils contaminated with only a few specific chemicals. The effectiveness of the technology is very limited for complex mixtures and for variable soil conditions. Soil flushing which is applied in situ through an injection/recirculation system, also has similar limitations. Both soil washing and soil flushing are ineffective for sites where contamination is deep (i.e., tens of meters below the surface).

Soil washing can be successfully applied for removing chlorinated hydrocarbon (3); however, its application to inorganic contaminants has been limited. One of the reasons for this limitation involves the mechanisms through which such contaminants are bound to soil particles. That is, organic contamination is generally bound to the organic content of soil, while inorganics may be bound through events such as ion exchange, chemical and physical adsorption, precipitation, or agglomeration. As yet, the technology for radionuclide removal is not fully developed. Soil washing offers a technology that should be considered for chlorinated hydrocarbon removal at DOE sites. However, its selection will depend on site-specific factors, minimum acceptable cleanup criteria, and cost-effectiveness, especially in comparison to other available technologies such as thermal desorption or microwave treatment. For radionuclide (U, Th, Ra) contamination, an assessment by the EPA has given soil washing a relatively high ranking for reliability and effectiveness, but the technology is assumed to be in the bench-scale (4) stage of development. Water, which is generally used as the washing liquid in soil washing, has many advantages. It is inexpensive, completely nontoxic, and can be used at ambient temperatures. The process can work well for water soluble radionuclide contamination such as uranium salts (chloride, sulfate, and hexafluoride). In other cases, additives, such as mineral acids or inorganic salts, may be necessary. For example, radium sulfate is almost insoluble in water but is soluble in sulfuric acid. A broad range of inorganic salt solutions can be used to remove radium and thorium from mill tailings and soils. In other instances, complexing agents, such as ethylenediamine tetracetic acid (EDTA) may be used.

The success of soil washing actually relies on size classification and the separation technologies, because it is not cost effective to continue to rewash the soil fines. <u>Physical separation technologies</u> that can be used in conjunction with soil washing have been long established in the mining industry and have also been field tested in soil washing systems. These physical separation technologies are described below.

> <u>Screening</u> is the mechanical separation of particles on the basis of size. Several classifications of screens exist, depending on the motion of the screen with respect to the particles. The major types of screens are the stationary grizzly (conventional and

probability); roll grizzly; sieve bends; trammel, centrifugal, and probability revolving screens; inclined, horizontal, and probability revolving screens; shaking screens; and reciprocating and gyrating screens. Screening is an inexpensive separation method, but screens may plug or break.

Classification is the separation of particles according to their settling rate in a fluid, depending on density and size. The three types of classifiers are hydraulic, mechanical, and non-mechanical. Hydraulic classifiers introduce air or water so the direction of flow opposes that of settling particles. Examples of hydraulic classifiers are the pocket classifier, as well as the cone, bowl, and cylindrical tank hydraulic classifiers. In mechanical classifiers, slow-settling particles are carried away in a fluid overflow, while particles with a higher settling velocity are deposited on the bottom (or on the side in a centrifuge) and dragged against the flow of liquid by various mechanical means. Different types of mechanical classifiers are the rake classifier, spiral classifiers, drag classifiers, solid bowl centrifuges, and countercurrent classifiers. Nonmechanical classifiers rely on gravitational or centrifugal force to separate particles. The hydrocyclone, settling cone, and elutriator are three commonly used types of nonmechanical classifiers.

Flotation is a process where, fine particles are treated with chemicals called promoters or collectors, which render them air-avid and water-repellent. A frother chemical is added and the solution is agitated to produce bubbles. The air-avid chemicals become attached to the bubbles and rise to the surface, where they collect in the froth and are skimmed off. Flotation is the most economical method of separating particles in the 0.1- to 0.01-mm size range, if appropriate additive can be found. However, the process is complex and has higher operating costs than gravity separation equipment.

Gravity separation devices exploit differences in particle size and density, keeping a slight separation between particles to enable them to move relative to each other and separate into layers of dense and light minerals. Gravity separators are classified by the means by which they achieve this separation. Jig-type separators depend on a vertical oscillating motion; shaking concentrators and tables apply a horizontal motion; and gravity flow concentrators, such as sluices and troughs maintain space by flowing the slurry down an inclined surface. This process has proven to be highly efficient for a wide number of applications, and it works well with most soil types. Disadvantages of the technology include the need for clean water and the low handling capacity.

Dewatering technologies are needed to regulate water content during soil washing operations. These technologies can be broadly classified into sedimentation (gravity and centrifugal) and filtration (deep bed and cake filtration, multimedia filtration, pressure filtration, and screening). Two new filtration developments are electrofiltration and membrane separation.

In addition to the above, a newer technology specific to radionuclide contaminated soils involves soil sorters that have been field tested by AWC Lockheed. This system consists of a conveyor, radiation detectors, and one or more gates. When placed at the front end of a soil-washing system, soil sorters can divert clean soil encountered by excavation, thus reducing the volume of soil to be treated (and reducing the cost of treatment), or they can be placed at the finishing end to ensure that the soil meets cleanup guidelines. It can provide better sampling rates and data than site surveys. The computerized soil sorter was originally used in AWC's mobile soil-washing system to clean up the coral sands of Johnston Atoll, but may not be as useful for less granular soils that would be more difficult to separate (5).

Chemical Extraction Techniques

Chemical Extraction (Primary). Chemical extraction (primary) may use the following solvents:

- Water can be used for pretreatment for subsequent extractions, but in general it is not very effective.

- Inorganic salts can be effective for thorium and radium, depending on whether insoluble sulfates or hydroxides are present. Such an extraction would probably need large solution-to-solid ratios.

- Mineral acids, with relatively small liquid-to-solid ratios, render a high percentage of removal for radium, thorium, and uranium by using acid extraction with sulfuric, nitric, or hydrochloric acids. However, equipment and reagent costs are high, and the waste stream, which will likely be environmentally harmful, may be difficult to dispose of. Regulatory issues also need to be addressed. International Remediation Corporation has developed a pilot scale process that has been bench-scale tested for radionuclides. This process can be used to treat mixed wastes with low concentrations of radionuclides and heavy metals if biological pretreatment is used to remove organics before leaching the soil (1).

- Complexing agents, such as EDTA, CTA, or citrate, can remove radium. Although the reagent is expensive, it could probably be recycled and only low concentrations are needed. Equipment costs would probably be lower than for acid extraction, but a multistage system may still be needed.

Chemical Extraction (Secondary). Techniques to remove radionuclides from solvent extractants include:

- Precipitation and coprecipitation involves adjustment of pH and addition of chemicals and can be used directly on water and inorganic salt extraction liquor. This process can be operated in both batch and continuous mode and involves low capital cost. However, it involves a difficult, cumbersome, and costly operation that requires close control of operating conditions, especially for pH, which is not adaptable to automatic control.

Gaseous ammonia, NaOH, H_2O_2, or magnesia are added to precipitate or coprecipitate uranium.

- Solvent-solvent extraction involves transferring the radionuclides from the aqueous leach liquor to a nonaqueous dilutant by means of an extractant present in the latter that facilitates the transfer. This process is the preferred technology for extracting uranium from acid leach liquor, but it is not useful for carbonate leach liquors or high-solid content slurries. It can be performed as a continuous operation, is readily adaptable to efficient automation, and has better selectivity and versatility than ion exchange. Solvent extraction does have certain disadvantages. It cannot be used with carbonate leach solutions. The feed solution must be free of solids. Emulsion formation can be a problem, and loss of solvent to the leachate solution can cause environmental problems. Solvent reagents are very costly, and the process is more sensitive to the volume and grade of liquor than ion exchange. Extractants include alkylphosphoric acid, amines, tri-n-butyl phosphate (TBP), and trioctyl phosphine (TOPO). Frequently used dilutants are kerosene, fuel oil, toluene, and paraffins.

- Ion exchange is a highly selective method for uranium and radium recovery that can also be used to extract impurities before precipitation. Three types of ion exchange include fixed bed, moving bed, and resin-in-pulp. Ion exchange is an excellent and economic method for removing very fine radioactive contaminants from liquids, and it has been used to remove uranium at Fernald with good results.

  To recover uranium, strong and intermediate base anionic resins are loaded from a sulfuric acid or carbonate leach solution, and then are stripped with a chloride, nitrate, bicarbonate, or ammonium sulfate-sulfuric acid solution. The main limitations are that impurities can overload the circuits, and metals can poison the resin, thus reducing its life. Ion exchange resins, which can no longer be generated, can be incinerated, oxidized, or otherwise chemically destroyed to reduce waste before disposal. Encasing the resins in concrete, although seemingly a simple method of disposal, must be carefully studied to ensure the stabilization material is compatible. Otherwise, the resins may react and swell or shrink, causing cracking and/or loss of integrity in the encapsulation material.

- ACT*DE*CON is an extractant process developed by Bradtec Limited (UK) that uses variations of established solvents, modified to selectively decontaminate soil. The process can be applied in situ or ex situ. The contaminants are dissolved by the solvent and recovered by either selective ion exchange or evaporation. The dilute, aqueous-based extraction process includes contaminant recovery and solvent regeneration. It uses various site-adapted facets of carbonate recovery chemistry plus a chelant and an oxidant to chemically remove radionuclides. For example, oxidizing Uranium(IV) to Uranium(VI) allows formation of soluble carbonate complexes.

Ex-situ treatment uses counter-current extraction with multiple extractors. Contact time and number of extractors depends on the soil, contaminant, and decontamination level desired.

Decontamination factors of 10-20 are typically achievable. The solvent is regenerated by selective ion exchange, which necessitates a pretreatment such as thermal desorption if organics are present, or evaporation. Dissolved carbonate complexes can be recovered by anion exchange and then by elution in nitric acid. When organics are present, evaporation can be used, or a treatment process (PO*WW*ER, provided by Chemical Waste Management) can be used to concentrate wastes and catalytically oxidize any recovered volatile and semivolatile organic contaminants.

For in-situ treatment, the process of dissolution, recovery, and reconditioning is basically the same, but the recovery step must be modified to accommodate high flow rates and the presence of soil fines in the recirculating solvent. Soil would be flushed with dilute solvent, which would be recovered by horizontal recovery wells. The possibility of soil fines leads to the use of magnetic separation, rather than anion exchange or evaporation, for recovery. Composite particles, 1-3 microns in size, consisting of magnetite and organic polymers, bind to the contaminants and enable them to be removed from the solution by magnetic filtration and to be separated from the binding particles, thus enabling their reuse.

The advantages of this method are that it can be applied in situ as well as ex situ, and it has lower costs than acid leaching or soil washing. It can be used on soils that contain high percentages of fines and cannot be treated by conventional soil washing. However, consideration of its application must be proceeded by site- and contaminant-specific feasibility studies. The process has been tested at the Nevada Test Site. It can remediate soils contaminated with uranium, plutonium, americium, thorium, radium, barium, and lead, as well as process vessels, hot cells, and vehicles contaminated with depleted uranium. The waste generated from this process includes the eluted/precipitated carbonate complexes in the form of sludge or filter cake. These wastes could be dewatered and used as feed to form a glass, ceramic, or concrete monolith waste form (1).

Soil Washing Technologies - Combinations of Physical Separation

These systems of technologies use physical and chemical separation techniques to reduce the volume of contaminated soil. The usual results are that the contamination partitions into one or another fraction of the soil, typically onto particles of smaller sizes such as clay or silt. Attrition of particle surfaces by agitation or grinding can help remove surface contamination from larger particles. Changes in redox potential, surfactants to solubilize hydrocarbons, and biological treatments can also be useful when dealing with mixed wastes.

Depending on characteristics specific to the site and contaminant chemistry, these systems of technologies can be useful in reducing the volume of contaminated soil. Under the best of circumstances, the contamination activity will be partitioned to a small fraction of the soil. The rest of the soil, with contamination activity reduced to a reasonable level, can be replaced in the area from which it was removed. However, it is important to understand the fixation mechanisms through which contaminants are held onto soil particles. While many inorganic contaminants are generally held in soils by physical adsorption or cation exchange, this is by no means universal.

Binding can also occur through precipitation, agglomeration, substitution in mineral lattice, stabilization by free organic ligands, or through biological activity. An understanding of the soil chemistry is the key, and acidity, alkalinity, organic content, and the fines fraction all are important characteristics. Highly humic soils tend to keep metals soluble because of their acidity, but they also have generally high cation exchange capacity. Thus, mechanism-specific leachant solutions can be engineered.

Site- and contaminant-specific bench- and pilot-scale testing are necessary before a full-scale system can be put into operation, since the choice of additives and unit operations may be different for each site. If an acid is used, the wash could produce additional secondary waste that must be dealt with, and the wash must be decontaminated if it is to be recycled. Contaminants may not partition adequately to allow any part of the soil to be considered decontaminated, and/or the fraction of the soil that contains the contaminants could make up a large percentage of the total (more than 25-35%), thus making volume reduction insignificant.

Soil washing is most useful when the contamination is contained largely by a small fraction of the soil. Often, however, contaminants adsorbed onto large fragments of soil can also be removed by scrubbing processes. Soil fractions such as silt, clay, and possibly process water or off gas, may need to be disposed of, although the latter two can often be treated and recycled. Process water that undergoes physical or biological treatment can generate tertiary waste. Fine fractions often need dewatering (osmotic or otherwise) before off-site disposal, stabilization, or vitrification. This technology may be combined with other processes such as soil calcining, aggressive chemical oxidation of soil fines, and vitrification (6).

The types of technology systems that have been developed are reviewed below.

Soil Washing and Physical Separation washes the soil with chemical solutions, then separates coarse and fine particles (e.g., Rocky Flats plutonium treatment plant). This technology is applicable where radioactive contaminants are closely associated with fine soil particles. It is simple, relatively inexpensive, and should require no major process development. However, it may not work for humus soil or highly contaminated soil.

Separation and Chemical Extraction separates the soil into coarse and fine fractions. The coarse fraction, assuming it is not quite to the "clean" level, would be acid leached, stripped by solvent extraction, and then separated by precipitation and/or ion exchange. The fine fraction would be combined with the extracted radionuclides. Alternately, a two-stage acid leaching can be used, or, if the coarse fraction is relatively "clean," the fine fraction can be leached instead. This technique can be used for clayey, sandy, and humus soils. Soil with higher levels of radioactivity can be treated, but this method is expensive and has involves chemical usage. Separation and chemical extraction needs further development for use with radium, and it may not be able to extract uranium, thorium, and radium in a single process.

Separation, Washing, and Extraction separates the contaminated soils and scrubs them with washing fluids before chemical extraction. Agents that can be used for washing include surfactants, chelating agents, and acid or alkaline solutions. This technology could be used for granular soils, but clay and humus soils would probably be difficult to clean by countercurrent extraction (7)

APPLICABILITY TO DOE SITES

Oak Ridge Reservation: As discussed earlier, soils at the Oak Ridge Reservation are highly clayey and silty. Contamination at the site includes U, Hg, oil/grease, and other contaminants. Soil washing does not appear to be a feasible technology. Efforts to develop in-situ vitrification technologies are in progress at this site (8).

Rocky Flats: Radionuclide contamination at Rocky Flats includes U, Pu, and Am. During the 1970s and 1980s, Rockwell International conducted extensive technology development work in a number of techniques, including dry screening, wet screening, ultrasonics, chemical oxidation, calcination, desliming, flotation, and heavy-liquid density separation (9-11). Wet screening of soils appeared to be successful in decontaminating >4-mm soil fractions to levels of <5 dpm/g of Pu and Am. A study was conducted to determine the influence of several additives (Calgon, Basic - H detergent, Turco 4342 detergent, citric acid, oxalic acid) in the wash water on the efficiency of soil washing. The soil samples were contaminated with Pu, Am, lathe coolant oil, and carbon tetrachloride. Wet scrubbing worked successfully, and filtered solutions remained relatively free of activity. Wet screening with water was effective in decontaminating 65% of soil tested (>2.4-mm fraction) to <6 pCi/g of Pu. Contamination levels in original soil ranged from 900 to 140,000 pCi/g of Pu. Given the success of these tests and the nature of the soil (sandy gravelly loam), it is clear that soil washing is an applicable technology for Rocky Flats soils. Further feasibility studies may be necessary to review specific soil systems that are commercially available.

Hanford Site: Soil washing for remediating soils contaminated with radionuclides and heavy metals is being considered at the Hanford Site. The soils are typically up to 90% sand, gravel, and cobbles. Previous limited assessments have shown that it is possible to achieve a high degree of decontamination of the coarse fractions of the soil. However, significant variations were found in the partitioning of radionuclides and heavy metals between the coarse and fine soil fractions at any one site. Bench-scale soil washing tests have confirmed previous results (12). After washing, contamination partitions preferentially to the <250 micron fraction, but the extent of decontamination of the coarse fraction varies greatly between soils. Because of the local geology and the types of contamination resulting from operations conducted at the Hanford site, contaminated soil conditions are unique. Besides the radioactive contaminants (U, Sr, Cs, Pu), heavy metals, nitrate and sulfate salts, organics, and mixed waste are also present. It appears that applicability of soil washing at Hanford would be in treating near-surface soils contaminated with inorganic materials. Due to the chemical form of the contamination present, further testing is necessary to evaluate soil washing as a potential technology.

Specific soil washing systems would require feasibility testing.

Fernald: A number of preliminary tests (conducted at Oak Ridge National Laboratory) for uranium removal from soils at Fernald showed that detergents and nonionic surfactants were ineffective (13). Mild acid wash (0.1 N nitric acid) was effective in removing uranium precipitate on the soil and dissolving some uranium associated with carbonates. The NaOCl was found to be an effective oxidant for a reduced form of uranium. The EDTA was found to be an effective chelating agent for some of the soils. An examination of the soil fraction data shows that a significant percentage of soil particles is <1-mm size fraction. Even though particle size distribution varies with location of soils, at certain locations more than 50% of soil particles are <0.05-mm size fraction. Characterization tests recently conducted for the integrated demonstration at the site indicated that uranium was present primarily in particulate form, either as discrete individual particles or cemented to silt, sand, or gravel fractions of the soil. Thus, size-based separation would not decrease waste volume significantly. The most effective treatments were found to be heavy liquid density separation for the particulate uranium, and citric acid and ammonium carbonate treatments for adsorbed uranium(13). As a part of the Minimum Additive Waste Stabilization (MAWS) demonstration program, a soil washing system is being developed by Lockheed Environmental Systems and Technology Company. The results of this demonstration will define the extent of applicability of soil washing to Fernald soils.

Savannah River Site: Soils at the Savannah River Site contain 10-50% clay content. In 1976, a series of tests were conducted for Pu removal from the soils by agitation with water (14). At predetermined flow rates, some partitioning of particles according to size was observed during the washing. Results showed that increased scrubbing time both increased the amount of material in the silt-clay fraction and decreased the amount of contamination in the sand fraction. Ninety-five percent of the contamination partitioned with the silt-clay fraction. However, because the soils at the site are mostly clayey, significant volume reduction is not feasible. Soil washing does not appear to be an applicable technology at this site. Bench- and pilot-scale feasibility studies of any specific commercial system will be necessary to assess its applicability.

Commercial Systems[1]

Information about the following systems was gleaned from EPA (1,3-4) and other sources (12), as well as from company fact sheets. Details of the technologies should be accessed directly from the vendors.

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[1] Mention of these commercial systems does not indicate an endorsement by the authors or their organizations.

Biotrol: This system uses intensive scrubbing technology and may include mixing trommels, pug mills, vibrating screens, froth flotation cells, attrition scrubbing machines, hydrocyclones, screw classifiers, and dewatering operations. The process may use chemical agents such as surfactants, detergents, chelating agents, pH adjustment, and heat. The three mechanisms that may come into play are (1) dispersion and separation of contaminated fine particles, (2) scouring of coarse particle surfaces, and (3) dissolution of contaminants. To our knowledge, this system has not dealt with radionuclides.

Westinghouse: This system treats radionuclides, heavy metals, and organics. It uses attritition scrubbing, size separation, and chemical extraction. Size separation, the addition of a surfactant, and extraction with a combination of NaOCl and Na_2CO_3 were successful in cleaning sewage sludge and oily landfarm soil contaminated with uranium, mercury, and PCB.

AWC, Inc.: The process has been pilot- and field-scale tested for radionuclides. The TRUclean process is used for Pu, U, Ra, Th (tried at FUSRAP sites, Rocky Flats, Oak Ridge Y-12, and Fernald). Pilot plant testing has been conducted at the Nevada Test site. Contaminated soil is fed to a trammel screen to separate oversized soil pieces, which are monitored to detect contamination. Contaminated oversized fragments are crushed and passed through the trammel screen, as are fines and contaminants. Radioactive or heavy metal contaminants have densities on the order of 6-18 g/cm^3, while soils have specific gravities in the range of 2-3 g/cm^3. Agitation via a pulsed pressure wave in the gravimetric separator causes the denser particles to separate and be captured, while the lighter soil particles go on to be dewatered and monitored for radioactivity. The process has successfully treated materials with as little as 2 g/cm^3 difference in specific gravity. When tested on coral sands, about 60% of the material processed was found to be "clean" of Pu-239 (below action level).

TechTran, Inc.: The process is in the field testing stage. It uses combined chemical binding and precipitation, as well as physical separation of radionuclides. The system can be used for cleanup of water, sludges, and soils (preprocessed into slurries) contaminated with radium, uranium, thorium, and heavy metals. Rapid turbulent mixing of the proprietary material, which is a fine powder consisting of complex oxides and other reactive binding agents, adsorbs, absorbs, and chemisorbs for coagulating, flocculating, or precipitating reactions. Water is then separated from the solids by (1) particle size and density separation with clarifier technology and microfiltration, and (2) dewatering, through use of a sand filter. The collected, stabilized filter cake, which consists of radionuclides, heavy metals, and other solids including the proprietary material (if it can not be recycled), is ready for disposal in a grout, cement, ceramic, or glass matrix.

Bergmann USA: The process is in full-scale operation and has been bench-scale tested on radionuclides. Soil washing operations consist mostly of physical separation methods. The company has built 20 full-scale transportable systems that process 5-350 tons of soil per hour and has completed 22 full-scale cleanups. Cost was mentioned in the range of

$75-$125 per ton. Unit operations include feed preparation, attrition scrubbing, size classification, desliming, thickening, gravity separation, clarification and water treatment, and dewatering. The process is economical for sites with more than 5,000 tons of material, with soil that has less than 40% fines (<63 microns) and 20% humus material.

The Netherlands: In the Netherlands, soil washing techniques have been used to wash organics and inorganics of various types, but not radionuclides(12). Heijmans has developed a semi-transportable soil washer capable of handling 10 tons per hour. The system has been in use since 1985 for removal of cyanides, low density hydrocarbons, and heavy metals (Cr, Cd, Ni, Pb, and Zn). Another system for similar types of contaminants is the HMZ process, which combines particle sizing, soil washing, and water treatment. The Heidemij system consists of screening, separation, froth flotation, sludge treatment, and residuals management. Another process, BSN (Bdemsanering Nederland), uses a high-pressure water jet system that was originally developed to separate oil from sandy soil.

In addition to the above vendors, other companies involved in developing soil washing technology include Bio-Recovery Inc.; Canonie Environmental Sonics Corporation; Environmental Technology Application; Flo Trend System, Inc.; Geochem, Inc.; Northwest Enviroservice, Inc.; OHM Corporation; On-Site Technologies, Inc.; Battelle PNL; Roberts & Schaefer Company; Scientific Ecology Group, Inc.; Warren Spring Laboratory (England); and Waste-TechSonics, Inc.

The EPA's VISITT database currently lists 15 companies involved in the development of soil washing systems, with four in the bench-scale testing stage, seven in pilot testing stage, and four with fully developed products. It should be noted that participation in the VISITT database is voluntary, and not all companies have submitted profiles to the database.

While evaluating these technologies for potential application at a site, these questions are important to address:

1. Which process is best suited for which contaminants?
2. What problems will be encountered in achieving regulatory compliance?
3. What are the needs for further development, testing, and demonstration in order to implement these technologies?

Remediation of complex sites requires complex technological solutions and, generally, no single technology is sufficient. By necessity, trains of technologies must be considered, as in the example given below:

Radiologically → Capping and In-Situ Disposal
Contaminated Soil → In-Situ Grouting or Chemical Stabilization
→ In-Situ Vitrification → Retrieval → Geological Disposal
↓
Stay in Place
Land Encapsulation
Concrete Vaulting

→ Cementation → Geological Disposal
Ex-Situ Vitrification
Ceramics

Clean Soil
↑
→ Soil Washing → Screening/ Separation → Waste Immob. → Disposal
↓
Water Treatment → Clean Water

CONCLUSIONS AND RECOMMENDATIONS

One generic solution to site remediation does not exist. No single technology would work for all sites, or even for a single site or a single contaminant. Ultimately, radionuclides and mixed wastes must be safely and economically disposed of, with some type of treatment or immobilization processing. In essence, the technologies review showed that most remediation technologies must be considered in the form of a technology train. This idea is especially important because it is significant from a public perspective and there is a statutory preference for permanent solutions.

The applicability of soil washing to some of the DOE sites has been reviewed. Research and development are necessary in the site- and contaminant-specific context. Technologies such as wastewater treatment and dewatering technologies can help fill the gaps in technology trains. The application of any commercial system at a site will require feasibility studies. Volume reduction technologies, however, should continue to be developed to reduce the need for increasingly expensive disposal space.

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5/20/93