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SOIL WASHING TREATABILITY STUDY

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TABLE OF CONTENTS

List of Figures	iv
List of Tables	vi
List of Acronyms and Abbreviations	vii
1.0 Introduction	1-1
1.1 Purpose of the Soil Washing Treatability Study	1-1
1.1.1 Initial Screening of Alternatives	1-2
1.1.2 Soil Washing Description	1-3
1.1.3 Soil Washing Literature Review	1-4
1.1.3.1 Physical Separation	1-5
1.1.3.2 Chemical Extraction	1-6
1.1.3.3 Existing Soil Washing Systems	1-7
1.1.4 Study Justification	1-8
1.1.5 EPA Treatability Guidance	1-9
1.2 Nature and Extent of Soil and Soil Contamination	1-10
1.2.1 Soil	1-10
1.2.2 Soil Contamination	1-11
1.2.2.1 Operable Unit 5 Remedial Investigation	1-11
1.2.2.2 Uranium in Soil Integrated Demonstration Characterization Study	1-12
1.2.3 Description of Treatability Study Soil	1-12
1.2.3.1 Incinerator Area (ID-A)	1-12
1.2.3.2 Plant 1 Drum Storage Area (ID-B)	1-13
1.3 Description of Treatability Study Approach	1-13
1.3.1 Remedy Screening - Bench-Scale Testing	1-13
1.3.2 Remedy Selection - Pilot-Scale Testing	1-14
1.3.3 Relationship of Treatability Data to FS Evaluation Criteria	1-14
1.4 Description of Other Soil Washing Laboratory Studies	1-15
1.4.1 Oak Ridge National Laboratory (ORNL)	1-15
1.4.2 Lockheed Environmental Systems and Technology (LESAT)	1-15
1.4.3 Westinghouse Science and Technology Center (WSTC)	1-16
2.0 Conclusion and Recommendations	2-1
2.1 Conclusions	2-1
2.2 Recommendations	2-6
3.0 Treatability Study Approach	3-1
3.1 Study Objectives and Experimental Design	3-1
3.1.1 Study Objectives	3-1

3.1.2 Soil Washing Experimental Design	3-2
3.2 Soils Used in the Soil Washing Treatability Study	3-1
3.2.1 Initial Selection of Soil	3-2
3.2.2 Initial Analysis and Characterization of Soil	3-3
3.2.3 Laboratory Preparation and Initial Analysis of Soil	3-6
3.2.3.1 Total Uranium Analysis by Ion Chromatography (IC)	3-7
3.3 Bench-Scale Testing	3-7
3.3.1 Stage I: Physical Separation Tests	3-7
3.3.1.1 Test Objectives	3-7
3.3.1.2 Chemical Dispersant/Extractant Tests	3-7
3.3.1.3 Attrition Scrubbing Tests	3-8
3.3.2 Stage I: Chemical Extraction Tests	3-9
3.3.2.1 Test Objectives	3-9
3.3.2.2 Phase I: Initial Screening of Chemical Extractants	3-9
3.3.2.3 Phase II: Screening of Selected Extractants	3-11
3.3.2.4 Phase III: Time, Temperature, and Concentration Study	3-12
3.3.3 Stage II: Physical Separation and Chemical Extraction Tests	3-12
3.3.3.1 Test Objectives	3-12
3.3.3.2 Experimental Design Comparison Test	3-12
3.4 Pilot-Scale Testing	3-14
3.4.1 CRU5 Soil Washing Demonstration Tests	3-14
3.4.1.1 Test Objectives	3-14
3.4.1.2 Equipment Used in the Soil Washing Pilot Plant	3-14
3.4.1.3 Chemicals Used in the Soil Washing Pilot Plant	3-15
3.4.1.4 Soil Washing System Design and Operation	3-15
3.4.1.5 Analytical Support	3-21
3.5 Additional Soil Washing Process Testing for Other COCs	3-21
3.5.1 Test Objectives	3-21
3.5.2 Experimental Design and Procedures	3-22
3.5.2.1 Location of Additional Soil (AS) for Testing	3-22
3.5.2.2 Preparation and Initial Characterization of Additional Nine Soil	3-22
3.5.2.3 Simulated Soil Washing System Test	3-23
3.5.3 Equipment and Materials	3-23
3.5.4 Sampling and Analysis	3-23
3.5.5 Data Management	3-24
4.0 Results and Discussion	4-1
4.1 Initial Characterization	4-1
4.2 Bench-Scale Tests	4-1
4.2.1 Stage I: Physical Separation Tests	4-1
4.2.1.1 Initial Analysis and Characterization Soil	4-1
4.2.1.2 Chemical Dispersant/Extractant Study	4-4

4.2.1.3 Attrition Scrubbing Tests.....	4-6
4.2.2 Stage I: Chemical Extraction Tests.....	4-9
4.2.2.1 Initial Analyses and Characterization of Soil	4-9
4.2.2.2 Phase I: Initial Screening of Chemical Extractants	4-10
4.2.2.3 Phase II: Screening of Selected Extractants.....	4-11
4.2.2.4 Phase III: Time, Temperature, and Concentration Study	4-13
4.2.3 Physical Separation and Chemical Extraction Tests	4-15
4.3 Pilot-Scale Tests	4-16
4.3.1 Operable Unit 5 Soil Washing Demonstration Tests	4-16
4.3.1.1 Physical Separation	4-18
4.3.1.2 Soil Washing of the ID-A Soil.....	4-19
4.3.1.3 Soil Washing of the ID-B Soil	4-21
4.3.1.4 TCLP and Comparative HSL Analyses for Primary Process Streams ..	4-23
4.4 COC Tests	4-25

LIST OF FIGURES

1-1	Relationship Between Operable Unit 5 Treatability Studies To The RI/FS Process	1-9
3-1	Treatment Phases Of Soil Washing Experimental Design For Operable Unit 5 Soil	3-1
3-2	Initial Procedure For Preparing Soils Received At The Laboratory Prior To Initiating Bench-scale Testing	3-6
3-3	The Procedure For Attrition Scrubbing Tests	3-8
3-4	Phase I Of Remedy Screening Tests For Chemical Extraction Of ID Soils.....	3-9
3-5	Modified Phipps And Bird Stir Reactor	3-11
3-6	Phase II Of Remedy Screening Tests For Chemical Extraction Of ID Soils	3-11
3-7	Denver Equipment Company Attrition Scrubber	3-12
3-8	Stage II Of Remedy Screening Tests For Combined Physical Separation And Chemical Extraction Of ID Soils	3-13
3-9	3-Dimensional Computer Model Of The Soil Washing Pilot Plant-4 Views	3-16
3-10	A Process Flow Diagram For The Physical Separation Operations In The Soil Washing Pilot Plant	3-17
3-11	A Process Flow Diagram For The Chemical Extraction Operations In The Soil Washing Pilot Plant	3-18
4-1	Map Of The FEMP Showing Location Of Twelve Soils Used In Treatability Testing	4-2
4-2	The Effect Of Sodium Pyrophosphate Concentration And Attrition Scrubbing Time On Uranium Concentration Of Two Particle Size Fractions For ID-A Soil.....	4-7
4-3	The Effect Of Ammonium Carbonate/Bicarbonate Concentration And Attrition Scrubbing Time On Uranium Concentration Of Two Particle Size Fractions For ID-A Soil.....	4-8

4-4	The Effect Of Sodium Carbonate/Bicarbonate Concentration And Attrition Scrubbing Time On Uranium Concentration Of Two Particle Size Fractions For ID-A Soil	4-8
4-5	The Effect Of Sodium Pyrophosphate Concentration And Attrition Scrubbing Time On Uranium Concentration Of Two Particle Size Fractions For ID-B Soil	4-9
4-6	The Effect Of Ammonium Carbonate/Bicarbonate Concentration And Attrition Scrubbing Time On Uranium Concentration Of Two Particle Size Fractions For ID-B Soil	4-10
4-7	The Effect Of Sodium Carbonate/Bicarbonate Concentration And Attrition Scrubbing Time On Uranium Concentration Of Two Particle Size Fractions For ID-B Soil	4-10
4-8	Uranium Concentration In ID-A And ID-B Extracted Soils For Twelve Extractants	4-11
4-9	The Percent Of Total Uranium In Extracted Soil Solids, Spent Extract, And Rinsate For ID-A Soil Following Extraction For Twelve Extractants	4-11
4-10	The Percent Of Total Uranium In Extracted Soil Solids, Spent Extract, And Rinsate For ID-A Soil Following Extraction For Twelve Extractants	4-12
4-11	The Concentration Of Total Uranium In Extracted ID-A And ID-B Soils Following Chemical Extraction For Five Concentrations Of Sulfuric Acid	4-12
4-12	The Concentration Of Total Uranium In Extracted ID-A And ID-B Soils Following Chemical Extraction For Five Concentrations Of Nitric Acid	4-13
4-13	The Concentration Of Total Uranium In Extracted ID-A And ID-B Soils Following Chemical Extraction For Five Concentrations Of Hydrochloric Acid	4-13
4-14	The Percent Uranium Concentration In Extracted Soil, Spent Extractant, And Rinse Water For ID-A Soil Following Extraction With Five Concentrations Of Sulfuric, Nitric, And Hydrochloric Acids	4-14

4-15	The Percent Uranium Concentration In Extracted Soil, Spent Extractant, And Rinse Water For ID-B Soil Following Extraction With Five Concentrations Of Sulfuric, Nitric, And Hydrochloric Acids	4-14
4-16	The Effect Of Nitric Acid And Sulfuric Acid Concentrations, Temperature, Extraction Time, And Dose Rate On Uranium Concentration In Extracted ID-A Soil.....	4-14
4-17	The Effect Of Nitric Acid And Sulfuric Acid Concentrations, Temperature, Extraction Time, And Dose Rate On Uranium Concentration In Extracted ID-B Soil	4-15
4-18	A Comparison Of Residual Concentration Of Uranium In Two Size Fractions Of ID-A And ID-B Soils Following Attrition Scrubbing With A Deco Attrition Mill And A Hamilton Beach Mixer	4-16
4-19	Soil Washing Process Flow Diagram	4-17
4-20	The Sequential Reduction In Total Uranium Concentration In The 0.02 To 4.75 mm ID-A Soil Solids During Treatment Processes	4-20
4-21	The Sequential Reduction In Total Uranium Concentration In The Less Than 0.02 mm ID-A Soil Solids During Treatment Processes	4-21
4-22	The Sequential Reduction In Total Uranium Concentration In The 0.02 To 4.75 mm ID-B Soil Solids During Treatment Processes	4-23
4-23	The Sequential Reduction In Total Uranium Concentration In The Less Than 0.02 mm ID-B Soil Solids During Treatment Processes	4-23

LIST OF TABLES

3-1	Parameters For Initial Baseline Characterization.....	3-4
3-2	Test Program For ID Soils Extractant Screening.....	3-10
3-3	ICP Metals Analyzed During Combined Physical Separation And Chemical Extraction Testing	3-13
4-1	List Of Twelve Soils Showing Location Within The FEMP, Acronym Identifier, Initial Total Uranium Concentration, And Whether Other COCs Were Present	4-1
4-2	Geotechnical Parameters For ID-A And ID-B Soil Received By The Laboratory From The FEMP Site	4-3
4-3	Concentration And Distribution Of Total Uranium In Selected Particle Size Fractions Using A Soil/water Slurry ^a For ID-A And ID-B Homogenized Whole Soils From The FEMP Site	4-4
4-4	Particle Size Distributions And Uranium Concentrations For The Less Than 2-mm ID-A And ID-B Soils Resulting From Water And Four 1mM Dispersing Reagent Solutions	4-5
4-5	Concentration And Distribution Of Uranium In The Three Size Fractions Of The Less Than 2mm ID-A And ID-B Soils Using Water And Dispersants	4-6
4-6	Soil Washing Pilot Plant Process Streams For Incinerator Area Soil (ID-A, Run 1), Single Batch (Drum) Process	4-19
4-7	Soil Washing Pilot Plant Process Streams For Incinerator Area Soil (ID-A, Run 2), Single Batch (Drum) Process	4-20
4-8	Soil Washing Pilot Plant Process Streams For Plant One Pad Area Soil (ID-B, Run 1), Single Batch (Drum) Process.....	4-21
4-9	Soil Washing Pilot Plant Process Streams For Plant One Pad Area Soil (ID-A, Run 2), Single Batch (Drum) Process	4-22
4-10	Uranium Values By Two Laboratories For Both The ID-A And ID-B Soils Processed Through The Soil Washing Pilot Plant	4-24
4-11	Uranium Concentrations In The Soil Solids And The TCLP Extract For Six Femp Soil Before Treatment And Following An Acid And A Carbonate Extraction Process	4-25

1.0 INTRODUCTION

1.1 Purpose of the Soil Washing Treatability Study

Soil washing was identified as a viable treatment process option for remediating soil at the FEMP Environmental Management Project (FEMP). Little information relative to the specific application and potential effectiveness of the soil washing process exists that applies to the types of soil at the FEMP. To properly evaluate this process option in conjunction with the ongoing FEMP Remedial Investigation/Feasibility Study (RI/FS), a treatability testing program was necessary to provide a foundation for a detailed technical evaluation of the viability of the process. In August 1991, efforts were initiated to develop a work plan and experimental design for investigating the effectiveness of soil washing on FEMP soil. In August 1992, the final Treatability Study Work Plan for Operable Unit 5: Soil Washing (DOE 1992) was issued. This document shall be referenced throughout the remainder of this report as the Treatability Study Work Plan (TSWP).

The purpose of this treatability study was to generate data to support initial screening and the detailed analysis of alternatives for the Operable Unit 5 FS. All units of measure are presented in a modernized metric system, the *Système International d'Unités* or SI. Based on characterization data (see Section 1.2), relatively large quantities of FEMP surface and subsurface soils contain above-background concentrations of radioactive constituents. To a lesser degree, nonradioactive contaminants may exist in conjunction with the radioactive contaminants. To address the cases where these contaminants are present at levels exceeding preestablished preliminary risk-based action levels, a number of process

options, including soil washing, were considered. This process option review and evaluation process is described in the Operable Unit 5 Initial Screening of Alternatives (ISA) (DOE 1993). After careful review of these process options, soil washing was selected as a promising technology warranting more rigorous technical consideration through the conduct of site-specific treatability studies. A primary consideration was to integrate the soil washing treatability technology being evaluated in this study with other similar technology evaluations being conducted for the remediation of Operable Unit 5 soil.

The TSWP outlines the objectives, procedures, and techniques for conducting screening of soil washing processes and conditions. Work objectives were defined in the TSWP in the context of FS considerations as follows:

- Proof of principle for the soil washing technology's applicability to the FEMP soil
- Compliance of process option with applicable or relevant and appropriate requirements
- Projected mass and leachability data to support fate and transport modeling
- Residual concentrations of contaminants in the process streams
- Development of a pre-design process flow diagram and preliminary mass balance for a production-scale soil washing facility to facilitate detailed technical analysis and establishment of a sound basis for cost estimation
- Projected chemical, radiological, and physical characteristics of aqueous and solid process streams.

Soil washing, if successful, produces large volumes of remediated soil which potentially

can be returned to the site from which it was excavated while significantly reducing the final volume of material requiring greater confinement and disposal. The success of the process option will be assessed based on the final volume of treated soil and the level to which specific contaminants are removed. This volume reduction level will account for all processed soil, spent washing solutions, extracting chemicals, and the residues retaining significant levels of contaminants. Residues from this process may require selective treatment (e.g., vitrification or stabilization), storage, and/or disposal practices. In essence, the final volume of material requiring selective treatment, storage, and/or disposal practices must be significantly less than the initial volume of contaminated soil.

1.1.1 Initial Screening of Alternatives

An initial phase of the FS involves the development and screening of remediation alternatives, otherwise known as the ISA. Three of the primary steps in the ISA for Operable Unit 5 (DOE 1993) are (1) identifying and screening the technologies applicable to each general response action to eliminate those that cannot be technically implemented at the site; (2) identifying and evaluating technology process options on the basis of effectiveness, implementability, and relative cost to select a representative process for each technology type retained for further consideration; and (3) assembling the selected representative technologies into alternatives representing a range of treatment and containment combinations as appropriate.

The first step is identifying and screening the technologies applicable to each general response action. The general response action pertinent to treatability testing is the treatment response action. This includes physical, chemical, and biological measures which reduce the toxicity, mobility, or volume of a

contaminant or waste by altering the physical or chemical properties of the contaminant and/or media. The treatment process options identified and evaluated relative to effectiveness, implementability, and cost include biological, physical, physicochemical, solidification/stabilization, and thermal measures.

Assembling and selecting representative technologies into alternatives representing a range of treatment and containment combinations were presented in Section 4.0 of the ISA for Operable Unit 5. The following were the only technologies retained for further evaluation for each of the five treatment process options noted above:

- Biological - soil aeration
- Physical - soil vapor extraction
- Physicochemical - soil washing
- Solidification/stabilization
 - Cement-based/pozzolanic-based fixation
 - Microencapsulation
 - Batch vitrification/glassification
 - In situ vitrification
- Thermal - plasma centrifugal furnace.

The technologies for each treatment process option were then further evaluated in Section 5.0 of the ISA for Operable Unit 5, rating each according to: (1) effectiveness, (2) implementability, (3) capital cost, and (4) operation and maintenance cost. Three of the eight technologies (microencapsulation, in situ vitrification, and plasma centrifugal furnace) were not retained for further consideration. Soil aeration and soil vapor extraction were retained as a support option for limited soil areas. Two of the remaining three technologies (batch vitrification/glassification and cement-based/pozzolanic-based fixation) were already being evaluated under existing treatability studies for other operable units. Soil washing, considered a potentially viable

option with high implementability, was selected for further evaluation.

1.1.2 Soil Washing Description

Soil washing (generally referred to as soil decontamination) is an ex situ water-based treatment process that separates chemical contaminants from the soil matrix using a combination of physical and chemical treatments. The treatment technique basically mobilizes the contaminants physically by mass action, or chemically by complexing, chelating, reducing, oxidizing, or ion exchange mechanisms. Techniques like those used in solution mining and mineral extraction have been used in soil washing operations for the removal of contaminants from soil. The basis for this type of process is particle separation by size and/or density characteristics. Chemically amended aqueous solutions can then accelerate contaminant dissolution kinetics from individual soil size fractions.

There is a fundamental basis to soil that makes physical separation an important tool within the soil washing technology. Soil consists of organic and inorganic components. Organic components include vegetation (roots and shoots) and organic matter (partially decomposed vegetative material). Inorganic components consist of primary and secondary minerals. Particle-size separation is primarily directed at these mineral categories. The categories for coarse fragments (greater than 2 millimeters [mm] in diameter) and soil separates (individual-size groups of mineral particles less than 2 mm in diameter) have been defined by the U.S. Department of Agriculture (USDA), Soil Conservation Service. Soil separates include clay (less than 0.002 mm), silt (0.002 - 0.05 mm), and five categories of sand (ranging between 0.05 - 2 mm). Coarse fragments include gravel (2mm - 3 inches) cobbles (3 - 10 inches), and stones (greater than 10 inches). There may also be

materials within the soil, both natural and anthropogenic, that fall into the fragment categories that are termed debris.

Physical separation techniques have been the focal point of most soil washing processes and serve two objectives. The initial objective is to reduce soil aggregates to single-grain composition of clay, silt, sand, and gravel. This reduction is accomplished by either mechanical means (e.g., high pressure water or mixers) and/or chemical dispersing agents (e.g., sodium salts). This initial step in the operation is the basis for separating the coarse-size fraction of the soil (e.g., sand and gravel) from the finer particles of soil (e.g., silt and clay). The second objective of physical separation techniques is to dislodge chemical contaminants from the surface of soil particles by force and/or abrasive processes. High-pressure water washers (hydraulic shearing) and attrition scrubbers are two types of equipment to aid in these physical separation processes. Physical separation operations in soil washing may also include screening, centrifugation, froth flotation, hydrogravimetric separation (including hydrocyclones, mineral jigs, and spiral classifiers), and multigravity separation.

The concept of using these types of volume reduction processes for contaminated soil via physical separation techniques is based on the premise that the soil is primarily comprised of coarse particles and that most organic and inorganic contaminants tend to bind primarily to clay particles and, to some lesser degree, fine silt particles (see Section 1.2). However, there are soil/chemical matrices in which the chemical contaminants are associated with coarse silt and sand as well as the fine silt and clay. In these matrices, simple water-based physical separation processes may not remove contaminants from any size fraction to an acceptable level and combination of physical separation and chemical extraction processes

may be needed. This type of system would consist of first separating the soil into discrete-size fractions and then removing the chemical contaminants from each size fraction via physicochemical processes.

Although selected chemicals can be included in the physical separation part of the system, a separate part of the system may need to include a chemical extraction process.

Chemical reagents (especially sodium salts) which can be employed in the physical separation part of the system to break down soil aggregates into discrete soil particles may also function as extraction reagents, removing chemical contaminants from the surface of individual soil particles. However, more aggressive conditions (e.g., type of chemicals, chemical concentration, extraction temperature, and reaction time) may need to be incorporated into the chemical extraction part of the soil washing process to effectively remove contaminants from individual soil particles.

Water-soluble chemicals (e.g., surfactants, chelators, acids, and bases) can be used in specifically designed reactor vessels as part of the chemical extraction process. Water washing with extractive agents includes basic aqueous solutions (caustic, lime, slaked lime, or industrial alkali-based washing compounds); acidic aqueous solutions (sulfuric, hydrochloric, nitric, phosphoric, or carbonic acids); or solutions with surfactant or chelating agents. Hydrogen peroxide, sodium hypochlorite, and other strong oxidizing agents can chemically change the contaminants and enhance their removal from soil. The removal of organics from soil can be enhanced by strong basic or surfactant solutions, while the extraction of metals is best facilitated by chelating agents or strongly acid solutions.

Soil process streams resulting from the above-described physicochemical soil washing

system must be analyzed to determine the residual level of selected contaminants. Based on the amount of contaminants still remaining in each soil process stream, the soil is either released as final treated soil or recycled back through the soil washing system. The remaining residue and the part of the soil not effectively treated are collected, containerized, and stored for disposal or subsequent treatment (e.g., vitrification, solidification, stabilization, etc.).

A final operation in the soil washing system is the regeneration of the spent washing solution. In many operations, the amount of spent wash water generated during the soil washing operation may equal anywhere from three to ten times the initial volume of soil being processed through the system. To prevent the system from generating more waste than the initial volume of contaminated soil, regeneration of spent wash water is mandatory. Although innovative technologies for treatment of spent wash solutions exist (e.g., electromagnetic and biphasic separation), two primary processes for wastewater treatment are ion exchange and precipitation. The resin or precipitate (now containing the chemical contaminants removed from the soil and subsequently from the wash water) is collected and stored for further treatment and/or disposal.

1.1.3 Soil Washing Literature Review

An initial review of the literature on the use of soil washing for removing radionuclides from soil was conducted in 1991 in support of the TSWP. This review indicated that the application of soil washing to radionuclide-contaminated soil was minimal. Since that initial review, the soil washing technology has evolved, resulting in a broader and better defined soil washing process, as described in Section 1.1.2. The recent interest to make this technology successful has been the primary

driver. In part, the development of the soil washing technology is needed to: develop a technology that reduces the volume of contaminated soil that would otherwise have to be excavated, containerized, and stored; provide a processed soil fraction that can be returned to an environment requiring a minimum of institutional controls; and develop a soil washing technology that can be more universally applied to a variety of soil-contaminant matrices. Based on this understanding of soil washing, the recent literature review focused on three primary aspects of the technology: (1) physical separation processes relative to soil washing; (2) chemical extraction processes relative to the soil-contaminant matrices; and (3) existing soil washing systems or pilot-scale tests.

1.1.3.1 *Physical Separation*

Physical separation processes have been the focal point of the soil washing technology. Physical separation processes serve to: separate the soil into various particle size fractions; separate loosely bound contaminants from the soil; and separate particulate contaminants from soil particles. The concept of reducing soil contamination through the use of particle-size separation is based on the understanding that many organic and inorganic contaminants tend to bind primarily to clay and fine silt soil particles. The attraction of chemicals to this soil-size fraction (especially in ionic form) is primarily a function of the negative exchange sites associated with the surfaces of clay. Separating this soil-size fraction from the rest of the soil will in turn separate chemicals associated with the clay from the rest of the soil. In essence, this is called volume reduction, where a large mass of contaminant-free coarse soil particles is separated from the contaminant-laden finer fraction. There are occurrences where coating of clays, metal oxides, and carbonates on the surface of coarse soil separates and fragments

results in the larger size particles also containing significant levels of contaminants.

Some contaminants, especially metals, may reside in the soil in particulate form. Discrete particles of metals (e.g., uranium, lead, iron, etc.) may exist as either metallic products from manufacturing processes or have complexed into metal oxides, hydroxides, and carbonates. These particulates may exist in the soil as: free particulates that disassociated from individual soil particles; particulates that are bound to the surface of coarse separates and fragments; or particulates that are occluded within soil aggregates or soil particles. Liberating these particulates so that they are disassociated from soil particles is a primary function of physical separation processes.

Much of the technology and equipment used during the physical separation stage in soil washing comes directly from the mining industry. Pretreatment processes are initial steps in the soil washing operation and are designed to reduce soil aggregates to single grain composition (i.e., clay, silt, sand, gravel, cobble, rock, debris, and particulates). This is accomplished by a number of mechanical processes (e.g., grizzlies, trommel screens, and drum washers). High pressure water and/or mixers can also be employed at this stage to aid in particle liberation. Various screening mechanisms and sizes are used during these initial operations to perform particle sizing and separation. Generally, soil fragments and debris are removed at this point from the excavated soil because they constitute a small amount of the total soil mass, their size is not conducive to being processed through the subsequent steps of the operation without prior size reduction (crushing), and the level of contamination is not as high relative to the total mass in these oversized materials.

Once the excavated soil mass has gone through an aggregate dispersion process and

initial fragment and debris sizing and separation, the actual "boiler room" part of the physical separation process can begin treating the soil. Attrition scrubbers and mixing tanks are used to aid in particle and contaminant liberation. Additional particle-size and density separation processes are used to further physically separate soil particles. Selected mining equipment (e.g., froth flotation cells, clarifiers, hydrocyclones, mineral jigs, and spiral classifiers), centrifuges, and multigravity separators are used to perform various particle-size cuts of the soil separates. The resulting individual process streams, each containing a selected size of soil particle, can individually be addressed relative to further treatment or processing.

Certain particle-sizing equipment noted previously also serve as dewatering devices (e.g., centrifuges, hydrocyclones, and clarifiers). Dewatering processes are necessary to remove soluble contaminants from the soil solids and aid in further process operations requiring higher solids loading such as attrition scrubbing. Although filter presses and belt filters are sometimes employed for dewatering soil, the resulting filter cake (usually highly concentrated with contaminants) is considered a final process stream of the soil washing operation.

1.1.3.2 Chemical Extraction

The use of chemical reagents to displace ions or compounds associated with the soil's solid phase has been a subject of research since the inception of cation exchange. The incorporation of chemicals in an aqueous solution is used to physicochemically enhance the removal of ions and compounds (collectively referred to as chemicals) from soil particles. Physicochemical separation of chemicals may be via mass action, substitution, or complexation. The basic bonding mechanisms (e.g., ionic, covalent, nonspecific, polar bonding

and Van der Waal) forces will in part dictate the mechanisms by which these chemicals are disassociated from the solid matrix into the extracting solution. The chemical reagents used in the extracting solution will also in part be responsible for the selective disassociation of chemicals into the solution. The use of these water-soluble chemicals (e.g., surfactants, chelators, acids, and bases) can be incorporated into physical separation operations common to soil washing techniques, or they can be used in specifically designed reactor vessels as part of the chemical extraction process.

A review of soil washing technologies that use chemical extractants and their applicability to Superfund sites (EPA 1989a) concluded that water washing with extractant reagents is applicable for cleaning nonvolatile hydrophilic and hydrophobic organics and heavy metals from soil. The report concluded that, although extraction of organics and toxic metal contaminants from excavated sandy/silty soil that is low in clay and humus content has been successfully demonstrated at several pilot-plant test facilities, extraction from clay and humus soil fractions is more complicated.

Kunze and Gee (1989) demonstrated greater than 90 percent removal of a large number of contaminants from the soil at a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) site using various surfactant, organic solvent, and acid-washing solutions. They determined that both aqueous surfactant and aqueous citrate-based solutions are effective for high percentage removals of all classes of the organic compounds tested. Their bench-scale soil washing study also showed that with high levels of contamination at a site, several washings may be required and used solutions would have to be treated before reuse.

Soil washing is not a new technology, but its

application to mixed waste (organics, inorganics, and radionuclides) contamination problems, such as exist at the FEMP site, extend the application of such a technology to a relatively new dimension. Soil washing has been successfully used on soil contaminated with radionuclides. Richardson, et al. (1989), conducted soil washing studies on the removal of radium-226 and thorium-230 from two soil. The results of their wet-sieving and water-washing studies indicated that the combination of the two processes can significantly reduce the radionuclide levels in soil.

1.1.3.3 Existing Soil Washing Systems

Soil washing has been practiced in Europe since the mid-1980s and has received considerable attention in the United States during the 1990s. A review of soil washing vendors presented at the WASTECH™ Symposium indicated that there were 19 vendors in the United States and 14 in Europe. Although 14 United States vendors have conducted pilot-scale studies, only six vendors were noted as having full-scale soil washing systems. It has been noted that although pilot-plant demonstrations are designed to provide detailed cost, design, and performance data on a field-scale system, in some cases the system may become the actual plant used in site remediation.

Soil washing has shown up as the selected remedy in 17 records of decision (RODs) as of mid-1992. No full-scale systems were in operation in support of these RODs before 1992 (Mann 1992). A more recent literature search in support of the Operable Unit 5 FS has indicated that a number of full-scale demonstrations have been documented either through internal or referenced publications and news releases.

U.S. Environmental Protection Agency's (EPA's) Mobil Soil Washing System

The mobil soil washing system developed

during the 1980s separates contaminants from soil by high-energy mixing of soil with solvents, additives, surfactants, acids, and bases (Scholz and Milanowski 1983; Skinner and Bassin 1988; 1991). The soil washer consists of three components: a drum washer, a counter-current extraction chamber, and a dewatering unit. Soil is initially rough-screened to remove large stones and debris and then passed through a rotating drum equipped with high-pressure water sprays and a 2-mm screen. The countercurrent extraction chambers incorporate turbine mixers, air agitators, and hydrocyclones during the chemical extraction process. With a throughput capacity of approximately 2 tons per hour (tph), the system has been demonstrated at an Alabama site to treat lead-contaminated soil. Most recently, the system was demonstrated on soil at the Montclair/Glen Ridge Superfund site, initially characterized as containing radium-226 (Richardson, et al. 1990; EPA 1989a). Final results indicated that the system could treat over 50 percent of the soil mass to less than the targeted 15 picocurie per gram (pCi g⁻¹) activity level (Eagle, et al. 1993).

Alternative Remedial Technologies, Inc.

A joint venture in 1992 between Geraghty & Miller, Inc. and Heidemij Reststoffendienst has brought the Heidemij soil washing system to the United States. The system incorporates a combination of physical/chemical processes which first separate the oversize materials by a series of vibrating screens. Wet screening combined with particle-size separation using hydrocyclones creates a coarse fraction and a fine fraction. The coarse-grain fraction is directed to froth flotation cells where it is washed with chemicals before dewatering. The fine fraction is directed to a sludge basin where solids are allowed to settle and the resulting sludge is dewatered using a belt filter press. With a processing rate of 25 tph, the system has treated over 20,000 tons of soil contaminated with chromium, copper, and nickel at the King of Prussia Superfund site in

New Jersey.

Bergmann USA

The primary projects for Bergmann USA are a 10 tph demonstration plant for the Toronto Harbor Commissioners and a 10 tph barge-mounted plant for removal of polychlorinated biphenyl (PCB) contaminants from dredged sediment for the U.S. Army Corps of Engineers. The Toronto Harbor system incorporated a high-pressure trommel washer, attrition scrubbers, bioslurry reactors, and hydrocyclones for dewatering (EPA 1993). The treatment train was comprised of a trommel to remove oversize material, an attrition scrubber to segregate the soil into uncontaminated coarse material and highly contaminated fines, metals removal process by chelation, chemical and biological treatment for reduction of organic contaminants, and hydrocyclonic dewatering. The system achieved cleanup criteria for the gravel and sand products, representing about 80 percent of the product (treated soil), while concentrating 74 percent of the organic contaminants into 19 percent of the product output. The system was not effectively evaluated on metal removal due to low initial concentrations.

Lockheed Corporation

The Lockheed System incorporates a TRU clean™ patented modular process which includes soil size fractionation and gravimetric separation. The process has been demonstrated at the government-owned China Lake site in California, where particulate uranium was separated from a sandy soil. A combination of hydrocyclones and shaker screens was used to fractionate the soil into selected size groups (e.g., sand, silt, and clay). Modified mineral jigs were used to separate particulate uranium from the coarse soil fraction. Chemical extractants were subsequently used to remove residual nonparticulate uranium. Centrifuges are used for dewatering. Currently, a system incorporating hydrocyclonic/

shaker-screen size fractionation is located at the FEMP. This system also incorporates the use of attrition scrubbers, chemical extraction tanks, and dewatering centrifuges.

Westinghouse Soil Washing Process (WSWP)

The WSWP was used in 1992 for treating 16,000 cubic yards of metals-contaminated soil at a site near Bruni, Texas. Currently, the process is being tested at the Feather River Superfund site in northern California (ENR 1994). Contaminants at this site include pentachlorophenols (PCPs), polycyclic aromatic hydrocarbons (PAHs), dioxins, and heavy metals (arsenic, chromium, and copper). The full-scale units are integrated process trains which use equipment originally developed for the mining industry. The process is arranged to form three functional units: (1) an initial screening and washing of coarse materials, (2) breakup of the remaining solids followed by a thorough wash, and (3) a high intensity leaching and separation of the contaminated fines from the clean soil. The system is capable of treating soil contaminated with organics, heavy metals, and radionuclides.

1.1.4 Study Justification

The literature review conducted in 1991 for the TSWP resulted in few references on the removal of radionuclides from soil using a combination of physical separation and chemical extraction techniques. The review revealed that water washing with extractive agents is applicable for cleaning nonvolatile hydrophilic and hydrophobic organics and heavy metals from soil (EPA 1989a) and had been successfully used on soil contaminated with radionuclides. Information was not found on its application to soil containing the radionuclides, inorganics, and organics that characterize the Operable Unit 5 soil at the FEMP. Therefore, due to the lack of information available to adequately address the overall

effectiveness of the soil washing process on removing contaminants from the FEMP soil, as well as the other EPA remedy evaluation criteria necessary during the detailed analysis of alternatives, a decision was made to proceed with treatability testing. In August 1992, the final TSWP was issued and a treatability study was designed to evaluate the effectiveness of soil washing in removing contaminants, primarily uranium, from FEMP soil.

1.1.5 EPA Treatability Guidance

The EPA's Guide for Conducting Treatability Studies Under CERCLA (1989b) outlines a three-tiered approach to conducting treatability studies for a Superfund site. The revised approach and terminology (dePercin, et al. 1991) illustrated in Figure 1-1 is as follows:

- Remedy screening
- Remedy selection
- Remedy design

The three tiers of treatability testing are

divided into pre-ROD and post-ROD studies. The remedy screening and remedy selection testing are generally pre-ROD studies, and the remedy design studies are generally post-ROD. However, the appropriateness and levels of treatability testing required are flexible, and remedy design studies, on a site-specific basis, may be conducted before issuance of the ROD.

The remedy screening and remedy selection treatability studies provide the performance and cost data needed to evaluate all potentially applicable treatment alternatives and select an alternative for remedial action based on the nine RI/FS evaluation criteria. The detailed analysis of the alternatives phase of the RI/FS follows the development and screening of alternatives and precedes the actual selection of a remedy in the ROD.

Remedy screening is the first step in the tiered approach. The purpose of this step is to determine the feasibility of a treatment alternative for the contaminants/matrix of interest. These tests are typically conducted under conditions that are favorable to the technol-

FIGURE 1-1. RELATIONSHIP OF THE OPERABLE UNIT 5 TREATABILITY STUDIES TO THE RI/FS PROCESS.

ogy. These small-scale studies are designed to provide a qualitative evaluation of the technology and are conducted with minimal levels of quality assurance/quality control (QA/QC). Tests conducted under this tier are generic in nature (not vendor specific). If the feasibility of the treatment cannot be demonstrated, the alternative should generally be screened out at this time.

The purpose of the remedy selection tier is to generate the performance and cost data necessary for remedy evaluation in the detailed analysis of alternatives phase of the FS. The cost data developed in this tier should support cost estimates of +50 percent to -30 percent accuracy. The performance data will be used to determine whether this technology will meet remedial action objectives. Remedy selection studies are typically small scale, incorporating generic tests using bench- or pilot-scale equipment in either the laboratory or the field. The study costs are higher than those encountered in the remedy screening tier and the tests require longer durations to complete. The levels of QA/QC are generally moderate to high.

In the remedy design tier, detailed scale-up design, performance, and cost data are generated to implement and optimize the selected remedy (Figure 1-1). Remedy design studies are usually performed as part of remedy implementation on full-scale or near-full-scale equipment. These studies focus on optimizing process parameters, which are not a part of this treatability study.

1.2 Nature and Extent of Soil and Soil Contamination

1.2.1 Soil

Soil in the region was formed by parent materials that were deposited by the action of

Wisconsin and Illinoian glaciers. These materials consist mainly of glacial till but include sand, gravel, glacial lake clay, and silt.

Three major soil associations have been mapped in the vicinity of the FEMP by the USDA (USDA et al. 1980, 1982): Russell-Xenia-Wynn, Fincastle-Xenia-Wynn, and Fox-Genesee. The soil are usually light colored, acidic, and well drained. Many have developed on wind-blown material (loess), except along present and old river basins where the Fox-Genesee soil is glacial till origin. The soil are moderately high in agricultural productivity and are frequently used for growing cash crops and producing livestock.

Soil at the FEMP site are primarily categorized as Fincastle-Xenia silt loams. These soil are light colored, medium acid, and moderately high in productivity when properly managed. Moisture-supplying capacity is moderate, as are fertility and organic content. The soil have formed in 18 to 40 inches of wind-blown silt (loess) over limy loam till. In areas where Fincastle soil are predominant, artificial drainage is required for moderate crop productivity. If artificial drainage is not used, the water table remains high for extended periods in winter and spring. Fincastle-Xenia soil also cover large areas west of the FEMP.

Before development of the FEMP, soil in the former production area consisted primarily of Fincastle silt loams. The Fincastle series consists of deep, somewhat poorly drained soil that formed in loess and in the underlying loam till. Fincastle soil are characterized by low permeability, moderate productivity, seasonal wetness, and low soil strength. During the construction of the production area, native soil were covered by introduced gravels, paving materials, and facilities. Areas that are currently planted with grasses and maintained as lawns or buffer zones tend to

represent native Fincastle soil.

1.2.2 Soil Contamination

The nature and extent of chemical contaminants within FEMP soil has been investigated through two programs. The sampling and analyses conducted in support of the Operable Unit 5 RI/FS was extensive in describing the type of contaminants existing at the FEMP and the three-dimensional distribution of these contaminants throughout the soil profile. The Uranium in Soil Integration Demonstration (USID) program, established by the U.S. Department of Energy Office of Technology Development, is the second characterization program at the FEMP. The USID Characterization Task group was given the responsibility to conduct a study to obtain basic information relating to soil properties and the nature of uranium contamination for the site's soil.

Current characterization information indicates that a minimal amount of soil at the FEMP contains hazardous chemicals. However, constituents of concern (COCs) for contaminated soil at the FEMP, which have been noted in the Site-Wide Characterization Report (DOE 1993), are listed below:

<u>Chemicals</u>	<u>Radionuclides</u>
Antimony	Lead-210
Arsenic	Radium 226
Beryllium	Radium-228
Lead	Thorium-228
Mercury	Thorium-230
Aroclor-1254	Thorium-232
Aroclor-1260	Uranium (depleted)
Benzene	
DDT	
Tetrachloroethene	
Benzo(a)pyrene	

1.2.2.1 *Operable Unit 5 Remedial Investigation*

Uranium is the indicator parameter for contamination at the FEMP. Uranium has also

been present in samples containing concentrations above background levels for other inorganic constituents including radionuclides and metals, and concentrations above detection limits for organics. The level of contamination in surface soil is generally less than the level of contamination of soil under or near certain process buildings. The highest levels of uranium have been detected near Plant 6 and Plant 2/3. Acids were used to digest or pickle material in these locations. Organic contamination occurs near plants where chemicals were used for process development or in conjunction with machining and maintenance operations, except in the case of the fire training area, the graphite furnace and oil burner, and the coal pile.

Surface soil in the vicinity of the FEMP has become contaminated from a variety of sources. Overall, the site has received a dusting of airborne uranium from the stacks in the former production area. Additional airborne material has been released in the waste storage area by dust blown from the disposal pits and tracking of contamination by vehicles. The incinerator in the sewage treatment plant area was also a source of airborne contamination. Additionally, leaks and spills from processing activities within the former production area have resulted in soil contamination.

The data used to characterize the nature and extent of soil contamination at the FEMP were collected and analyzed from the spring of 1988 through 1990. In general, concentrations of total uranium in soil samples from outside the former production area and waste storage area are below 50 milligram per kilogram (mg kg^{-1}). The exceptions to this are in suspect areas, such as the fire training area, the sewage treatment plant area, and the rubble mound west of the K-65 silos. Each of these areas has surface contamination in excess of 50 mg kg^{-1} of total uranium. The

maximum total uranium value found in soil from throughout the former production area was detected in a sample collected just below the concrete floor of the Plant 6 wastewater treatment area.

Large portions of the former production area have total uranium concentrations in soil from 0.0 to 1.5 feet at greater than 50 mg kg⁻¹. Actually, a large part of the uranium contamination is a surface contamination problem. A comparison of the 50 mg kg⁻¹ contours indicates that below 1.5 feet total uranium values greater than 50 mg kg⁻¹ are restricted to the northern end of Plant 6, scattered points around the garage and heavy equipment building, the Plant 2/3 area, the southwest corner of the pilot plant, the northwest corner of the maintenance building, and the southeast corner of Plant 9. Within the former production area, leaks and spills from process equipment have resulted in deeper migration of contaminants at higher concentrations than is due to airborne deposition. Although uranium is the indicator parameter at the FEMP, many samples have been analyzed for other radionuclides. To better focus the investigation of this complex production network into a manageable technical framework, the former production area was separated into four distinct quadrants.

1.2.2.2 *Uranium in Soil Integrated Demonstration Characterization Study*

The primary objective of the USID program was to evaluate and demonstrate remedial alternatives for uranium-contaminated soil. An initial phase in this program was to obtain basic information relating to soil properties and the nature of uranium contamination. The USID selected five areas within the FEMP property and conducted an extensive characterization of selected soil samples from these areas (Lee and Marsh 1992).

The basis for this characterization was to investigate the nature of soil contamination by examining:

- Uranium distribution with soil depth
- Soil particle-size distributions and their uranium contribution
- Soil chemical and physical properties
- Particle density of soil and contaminant
- Mineralogical and microscopic properties of soil and contaminant
- Chemical leaching characteristics
- Background soil uranium content and soil properties.

The following results are taken directly from Lee and Marsh's report:

- Except in an area contaminated by acidic solution spills, the contamination depth of most areas was shallow (usually less than 10 centimeters [cm] containing from 10 to 2800 pCi g⁻¹)
- Background uranium concentration of off-site soil was less than 4 pCi g⁻¹
- The sand and silt-size fractions contained from 48 to 79 percent of the uranium in soil
- The dominant form of uranium was sand and silt-sized particulates often associated with calcium, phosphorous, iron, and silicon
- Most of the uranium particulates had a density greater than 2.9 grams per milliliter (g mL⁻¹)
- Considerable amounts of soil uranium, 10 to 40 percent and 20 to 75 percent, could be extracted using 2 percent solutions of ammonium carbonate and citric acid, respectively.

1.2.3 Description of Treatability Study Soil

1.2.3.1 Incinerator Area (ID-A)

This area is located outside of the production area to the east, and the underlying soil should be Fincastle series. The soil has a well-developed surface horizon with fine granular structure and the occurrence of small limestone gravel. The source of uranium contamination in this area was incinerator emissions from burning low-level contaminated trash.

1.2.3.2 Plant 1 Drum Storage Area (ID-B)

This area is located in the northwestern part of the production area and the underlying soil should be Fincastle series if they have not been too deeply disturbed. The soil had a weakly developed structure and about 30 to 60 percent limestone gravel. The presence of the angular limestone gravel indicated that the area had been highly disturbed from past activities. The source of uranium contamination in this area was runoff from the drum storage pad coupled with air deposition from stack emissions.

1.3 Description of Treatability Study Approach

The approach used for the Operable Unit 5 soil washing treatability study is illustrated in Figure 1-1. This approach was consistent with the EPA's tiered system for conducting treatability studies. The two-tiered treatability approach was designed to evaluate the soil washing process for Operable Unit 5 by conducting both bench-scale testing (remedy screening) and pilot-scale testing (remedy selection). A unique aspect to this standard CERCLA approach for conducting treatability studies is that the study was designed to support a cooperative testing effort between the USID program and the FEMP RI/FS project.

Parallel bench-scale tests were conducted during Stage I testing of the remedy screening

process. Because soil washing is a physico-chemical treatment process, separate physical separation and chemical extraction tests were conducted in a parallel effort. The physical separation tests were targeted as describing the particle-size distribution and the resulting uranium associated with each size fraction. The chemical extraction tests were used to identify the most effective chemical for separating uranium from the soil. Stage II incorporated the findings from Stage I testing into a combination of physical separation and chemical extraction treatments. The findings from these Stage I and II bench-scale studies were incorporated into a pilot-scale version of a soil washing treatment system during the remedy selection part of the CERCLA process.

The Guidance for Conducting Treatability Studies Under CERCLA (EPA 1988) recommends that target compounds be used during remedy screening tests. Because uranium is the primary contaminant at the FEMP, total uranium was selected as the target compound to evaluate the effectiveness of the various treatments tested. Although other contaminants were monitored during selected stages of testing, uranium was the primary analyte used to evaluate a treatment's effectiveness.

1.3.1 Remedy Screening - Bench-Scale Testing

The physical separation component of Remedy Screening-Stage I was designed to test the effect of different dispersants on removing uranium from different soil-size fractions and characterize the soil particle-size distribution and the respective uranium concentration among individual soil-size fractions. Each soil was dispersed in a number of sodium salt solutions and mechanically separated into specific soil-size fractions using a wet-sieving technique. Each soil-size fraction and spent dispersing solution was collected and analyzed

for total uranium.

In a parallel effort during Remedy Screening-Stage I testing, chemical extraction experiments were designed to test a wide range of chemicals under very aggressive conditions that were selected to give each chemical the best probability for effectively removing uranium from the soil. The conditions chosen were high temperature (80° C), relatively high reagent concentrations (e.g., 1:1), and relatively high dose rate (10:1). The high temperature and high reagent concentration may adversely increase the rate of other metal compound dissolution; therefore, the high dose rate will minimize the effect that common ion dissolution has on ionic strength of the extracting solution. The most effective extractants were determined by evaluating the residual uranium in the soil following extraction. These results would provide the baseline conditions to further define chemical selection and process optimization.

Stage II of the remedy screening process combined the results of Stage I physical separation and chemical extraction experiments. The soil-size fractions that were shown to retain significant levels of uranium were selected for use in a series of chemical extraction tests. The number of extractants tested during Stage I testing were reduced to only the most effective extractants in removing uranium from soil. During Stage II testing, the effects of extractant concentration, temperature, and dose rate were investigated. Also during Stage II testing, spent extractant treatment via precipitation and ion exchange were investigated. The uranium-loaded extractant solutions and rinse solutions contained material leached from the soil. Preliminary precipitation tests were performed to determine which type(s) of precipitating and flocculating reagents were necessary to remove the majority of the hazardous and radioactive metals. Ion exchange tests were

also performed to evaluate the effectiveness of specific resins in selectively and/or quantitatively removing uranium from the spent extractant and rinse solutions.

1.3.2 Remedy Selection - Pilot-Scale Testing

Pilot-scale testing of the soil washing process was conducted as part of the remedy selection component of the CERCLA guidance for treatability testing. The pilot-scale tests incorporated specific equipment (e.g., trommel, vibrating screen deck, attrition scrubber, centrifuge, and extraction vessels) as part of the soil washing system. Only the most successful chemical extracting solutions from Stage II bench-scale testing were incorporated into this system. It was expected that a combination of chemical extractants, combined with physical separation techniques, might be necessary to effectively remove uranium from the soil. The overall effectiveness of an empirically derived soil washing system for treating FEMP soil was evaluated by conducting a complete analysis of the soil before and following the treatment process.

1.3.3 Relationship of Treatability Data to FS Evaluation Criteria

The following information was obtained or can be calculated as a result of the treatability study testing:

- Volume of soil in which uranium content was reduced to defined concentrations for uranium and other COCs
- Volume of residues requiring disposal
- Wash water volume for treatment and/or disposal relative to the initial untreated waste volume
- Volume of extracting reagents for disposal relative to the initial volume of untreated waste
- Amount of contaminants removed from soil by extractants and process water

- Cost of implementing the technology
- Conceptual process flow diagram for a full-scale production system
- Conceptual mass balance across a process flow diagram (PFD) for full-scale production system
- Mobility of contaminants in untreated and treated soil.

1.4 Description of Other Soil Washing Laboratory Studies

1.4.1 Oak Ridge National Laboratory (ORNL)

Two soils were used in bench-scale testing at ORNL to determine the effectiveness of sodium carbonate and citric acid leaching (extraction) to decontaminate or remove uranium to acceptable regulatory levels (Francis, et. al. 1993). The information contained herein has been extracted from the abstract of their study. The objective was to selectively extract uranium using a soil washing/extraction process without seriously degrading the soil's physicochemical characteristics or generating a secondary waste form that would be difficult to manage and/or dispose of. The two soil used in the treatability testing were the same ID-A and ID-B soil from the incinerator area and Plant 1 storage pad area, respectively. These two soil were also used in an interlaboratory treatability study sponsored by the FEMP USID program. Uranium concentrations in these soil, as determined by ORNL, ranged from 450 to 550 mg kg⁻¹ total uranium.

Carbonate extractions generally removed from 70 to 90 percent of the uranium from the ID-B soil. Uranium was slightly more difficult to extract from the ID-A soil. Increasing the extraction temperature from 22 to 40° C for the ID-A soil increased the fraction of uranium extracted from approximately 40 to 80

percent. However, the increased extraction temperature did not appear to increase extraction effectiveness for the ID-B soil. Extraction with carbonate at high solution-to-soil ratios were as effective as extractions at low solution-to-soil ratios, indicating attrition by the paddle mixer was not significantly different than that provided in a rotary extractor. Pretreatment such as milling or pulverizing the soil sample also did not appear to increase extraction efficiency when carbonate extractions were carried out at elevated temperatures (60° C) or long extraction times (23 hours). Adding KMnO₄ to the carbonate extractions appeared to be more effective in removing uranium from the silt- and sand-size fractions (greater than 0.002 mm) of soil than from the clay-size fractions (less than 0.002 mm).

The most effective extraction rates (greater than 90 percent from both soil) were obtained using a citrate/dithionite extraction procedure designed to remove amorphous (noncrystalline) iron/aluminum sesquioxides from surfaces of clay minerals. Citric acid also proved to be a very good extractant for uranium. At pH values less than 5, approximately 50 and 90 percent of the uranium could be extracted from the ID-A and ID-B soil, respectively. A citric acid extraction (0.1 M) of the ID-A soil followed with two carbonate extractions containing KMnO₄ removed greater than 80 percent of the uranium, indicating that a combination of citric acid and carbonate extracting procedures may be the best approach for soil containing residual forms of uranium. ORNL's efforts to date have shown that significant quantities of uranium can be extracted from these two soil without seriously degrading the soil's physicochemical characteristics or generating a secondary uranium waste form that is difficult to manage and/or to dispose of.

1.4.2 Lockheed Environmental Systems and Technology (LESAT)

The bench-scale treatability testing conducted by LESAT was in support of the Minimum Additive Waste Stabilization program with the specific objective of demonstrating the feasibility of integrating vitrification of the Operable Unit 1 waste pit material with soil washing and water treatment. The initial objective of the soil washing system was to use physical separation processes to provide a silica feed for the vitrification process. A subsequent objective was to use physicochemical processes with the soil washing system to treat that fraction of the soil not serving as the silica feed to an acceptable cleanup level.

The soil used by LESAT during their bench-scale treatability testing was from the Plant 1 pad area. The soil was not the same soil that was screened and homogenized by the USID program and used in subsequent bench-scale testing by ORNL and International Technology (IT) Corporation. The soil received by LESAT contained surface vegetation (grass) and roots. Therefore, specific characteristics, e.g., organic matter content, particle-size distribution, and uranium concentration, may significantly vary from those characteristic described for the ID-B soil (Plant 1 pad area soil). The following are the primary conclusions resulting from LESAT bench-scale soil washing treatability testing:

- Uranium contamination is distributed throughout the soil matrix in levels above 35 pCi g⁻¹ and the majority of soil particles are less than 0.1 mm in size. Consequently it was concluded that physical separation techniques alone will not achieve the 35 pCi g⁻¹ criteria and achieve a significant volume reduction.
- The 100 mesh (0.149 mm) to 0.03 mm fraction has the highest silica content of the soil matrix as determined by concentration of SiO₂. It was therefore selected as a feed stream for the vitrification process. Because of its high SiO₂ content it is beneficial to

vitrification and reduces the need for additives.

- There is a significant amount of organic matter in the soil matrix. The organic matter has the highest activity levels relative to other soil fractions. Because processing the organic matter through the leach process will reduce leach performance and/or increase chemical usage and cost, it will be screened out of the soil matrix and fed to the melter. Initial vitrification tests have shown that this soil fraction is processable for vitrification.
- Carbonate leaching of the minus-0.03 mm fraction is effective in achieving the 35 pCi g⁻¹ criteria.
- The ion-exchange resins to be used in field tests are acceptable in removing uranium from the leach concentrate, allowing the water to be recycled for use in the soil washing system.

1.4.3 Westinghouse Science and Technology Center (WSTC)

The soil used in bench-scale soil washing treatability testing by WSTC were the two soil collected under the USID program, the incinerator area soil (ID-A) and the Plant 1 pad area soil (ID-B). WSTC tested the use of 0.2 molar (M) ammonium bicarbonate (NH₄HCO₃) solution alone and in conjunction with a oxidation pretreatment using two percent sodium hypochlorite (NaOCl) solution. Based on these test parameters, the following conclusions were reached:

- Removal of the uranium from both soil appears to be technically feasible by using a combination of ammonium bicarbonate and sodium hypochlorite solution and physical separation.
- The contamination in the ID-A soil was divided between a highly soluble form and a relatively insoluble form in soil fractions between 0.075 to 0.3 mm.
- The contamination in the ID-B soil was highly soluble and readily mobilized by the leachate.

2.0 CONCLUSIONS AND RECOMMENDATIONS

2.1 Conclusions

An extensive investigation into the application of soil washing as an effective remedial alternative for soil at the Fernald Environmental Management Program (FEMP) was conducted over the past three years. The investigation was initiated with a characterization study by Oak Ridge National Laboratory (ORNL) of uranium contamination at the FEMP. This characterization study concluded, based on the five areas sampled (Plant 2/3, plant 1 drum storage pad, drum baling area, incinerator area, and Plant 6), that uranium was distributed throughout all soil size fractions (gravel, sand, silt and clay). In addition, uranium in the soil was noted to exist as individual discrete particles or as smaller particles cemented to silt, sand, and gravel fractions rather than as a preferentially adsorbed form on clay minerals. Although particulate uranium was a dominant form in FEMP soil, the delta specific gravity was not great enough for multigravitational separation techniques to work effectively. Because of the ubiquitous distribution of uranium among all soil particles, physical separation techniques alone were considered to be ineffective in achieving a volume reduction in the soil mass or a significant volume reduction in the uranium mass. Therefore, an emphasis was placed on investigating the potential effectiveness of using physicochemical soil washing processes for treating FEMP soil.

Following the initial characterization effort by ORNL, the scope of the subsequent treatability studies was a two-year investigation which focused on removing uranium from FEMP soil using a physicochemical soil washing approach. This investigation was funded by two DOE programs: A remedial

investigation/feasibility study (RI/FS) -funded series of treatability tests by IT Corporation on both a bench- and pilot-scale; and an Office of Technological Development-funded integrated approach by Lockheed, Westinghouse, as well as an array of national laboratories including ORNL, Los Alamos National Laboratory and Argon National Laboratory. Although these two Department of Energy-funded programs adhered to different missions, the integration of their activities and the sharing of data and ideas generated during the extensive treatability testing created an interactive exchange that focused on the ultimate objective of removing uranium from FEMP soil to an acceptable residual level in terms of both mass and mobility.

This report has focused on the results obtained during the treatability testing by IT Corporation and the Fernald Environmental Restoration Management Corporation (FERMCO). The study was conducted as part of remedy screening and remedy selection testing in support of the Operable Unit 5 FS to evaluate remedial alternatives for cleaning soil at the FEMP site. The testing was conducted in accordance with CERCLA guidelines for conducting treatability studies. Although, reference has been made frequently to support studies, in particular ORNL's test results, data presented here relative to constituent concentrations and removal efficiencies, are solely a product of these tests. Comparison to other test data for the same soil, must be with the understanding of the inherent variability associated with any soil-contaminant matrices, regardless of how homogeneous. In most cases, tests were run without replication, which negates the association of any statistical reliability with the results. In the few cases where duplicate or more replications were conducted, statistical interpretations with

respect to the data were presented.

During the two-year duration of treatability testing in support of the Operable Unit 5 FS, 12 soils were characterized and to some degree used in subsequent treatability testing. Initially, soil from two of the five areas investigated by ORNL, incinerator area (ID-A) and Plant 1 drum storage pad (ID-B), considered to be representative of the soil-contaminant matrices at the FEMP, were selected and used in the treatability studies. These two soil contained no constituents of concern (COCs) other than uranium. Because the Treatability Study Work Plan (TSWP) was directed at testing a remedial technology that would address a range in soil-contaminant matrices, a third soil (from the maintenance building area [OU5-A]) containing other COCs besides uranium was also used in the initial bench-scale treatability studies. However, due to certain site constraints, only the ID-A and ID-B soil were used in remedy selection pilot-scale testing at the FEMP soil washing pilot plant. The nine remaining soil (not initially referenced in the TSWP) were collected and used in bench-scale testing at the FEMP during the final stages of the treatability study to determine if the proposed hybrid soil washing process used as the foundation for the Operable Unit 5 FS would be effective over a wider range of soil-contaminant matrices.

The two soil studied during initial bench-scale testing were the ID-A and the ID-B soil. Geotechnical characterization of the two soil (initially prescreened at 19 mm) showed that 77.4 and 74.6 percent, respectively, of the ID-A and ID-B soil were in the less than 0.05 mm-size fraction and of this percentage, approximately 15 percent was clay (less than 0.002 mm). It was also determined that uranium was distributed among all particle-size fractions (consistent with ORNL results). Soil quantities used during bench-scale testing contained approximately 497 and 450 mg kg⁻¹

total uranium for the ID-A and ID-B soil, respectively. Uranium concentrations in the sand and silt fractions were 1028 and 317 mg kg⁻¹, respectively, for the ID-A soil and 189 and 223 mg kg⁻¹, respectively, for the ID-B soil. Although the ID-A and ID-B clay fractions contained 1475 and 2710 mg kg⁻¹, respectively, part of this was uranium that was brought into solution during the soil dispersion process and adsorbed back onto the clays.

During Stage I of the bench-scale treatability studies, physical separation techniques and chemical dispersants/extractants were used in combination to treat the ID-A and ID-B soil. Four 1 mm sodium reagent solutions (sodium hydroxide, sodium carbonate, sodium bicarbonate, and a sodium citrate-bicarbonate-dithionite mixture) and potable water were evaluated for effectiveness in dispersing each soil into single-grain separates and extracting total uranium from each of the resulting particle-size fractions. Dilute sodium solutions were more effective than water in dispersing the soil. No solutions were effective in removing uranium from any soil-size fraction. The use of dispersants, as compared to water, on the less than 2-mm-size fraction seemed to cause a shift in the distribution of uranium out of the sand fraction and into the silt and clay fractions for ID-A soil and onto the clay fraction for the ID-B soil.

More rigorous treatment conditions were applied during the ensuing physical separation bench-scale testing. Attrition scrubbing was combined with higher strength sodium compound solutions and used to treat the less than 2 mm soil fraction for the ID-A and ID-B soil. The three alkaline extraction solutions tested were sodium pyrophosphate, sodium carbonate/sodium bicarbonate, and ammonium carbonate/ammonium bicarbonate. The independent variables tested were solution strength (0.1, 0.25 and 0.5 M) and attrition scrubbing time (5, 15, and 30 minutes). The

uranium concentration was determined in the sand fraction (greater than 0.053 mm) and the silt-clay fraction (less than 0.053 mm). There was little difference among the chemical extractants on their effectiveness in removing uranium from either soil fraction. Higher concentrations of each chemical extractant (0.5 M) were more effective in removing uranium from each of the two size fractions. Increasing the attrition scrubbing time from 5 to 30 minutes also increased the amount of uranium removed from each size fraction. Even though there was less than a linear response with increasing extractant concentration or attrition scrubbing time, a point of diminishing returns had to be selected. This point for Stage II testing would be a 0.25 M concentration for sodium carbonate/sodium bicarbonate and an attrition scrubbing time of 15 minutes. Sodium carbonate/bicarbonate was also selected due to its use in the uranium mining industry.

While the physical separation testing was being conducted, a parallel effort was being pursued with respect to the use of chemical extractants. Due to the ubiquitous distribution of contamination among all soil particles, 12 chemical reagents comprised of inorganic acids, salts, bases, and chelants were evaluated for their effectiveness in removing total uranium from the less than 2-mm-size fraction of the ID-A and ID-B soil. This remedy screening part of the study was designed in stages to selectively and sequentially investigate certain aspects of chemical extraction. Successful results from each stage were transferred to subsequent stages to further refine the use of chemicals for extraction of total uranium from both soil.

Stage I chemical extraction testing used very aggressive conditions. Very concentrated reagents were tested at a high extractant:soil ratio (10:1), high temperature (80°C) and a 4 hour reaction time. Results indicated that the

most effective chemical extractants in removing total uranium from both soil were the inorganic acids (nitric, hydrochloric, phosphoric, and sulfuric); they reduced total uranium concentration by over 95 percent. Although sodium carbonate, ammonium carbonate, and sodium hydroxide were more effective on the ID-B soil, all three extractants reduced total uranium concentration in the solids to less than 50 mg kg⁻¹, representing a more than 90 percent reduction in total uranium.

Based on findings from Stage I testing, three inorganic acids (sulfuric, hydrochloric, and nitric) were carried into Stage II testing for further investigation. Stage II testing was directed at reducing the half-concentrated acids used in Stage I testing to the lowest acid strength without reducing their effectiveness in uranium extraction. Stage II results showed that all concentrations of acids greater than or equal to 1 N were able to achieve less than 50 mg kg⁻¹ total uranium in the extracted soil solids, equating to a more than 90 percent reduction in uranium.

In Stage III testing, extractant, extractant concentration (1 and 2 N), temperature (ambient and 40°C), dose rate (4:1 and 7:1 extractant:soil), and extraction time (0.5 and 2 hours) were evaluated. Although nitric and sulfuric acid extractants were effective on both soil in removing uranium, sulfuric acid was selected for use in pilot-scale testing. Results from bench-scale testing showed that a 1 N sulfuric acid solution (4:1 dose rate) at 40°C and 0.5 hour extraction time was able to reduce total uranium concentration in the ID-A extracted soil to 38 mg kg⁻¹. Sulfuric acid was also very effective on ID-B soil, regardless of extraction conditions. A 1 N sulfuric acid solution, 0.5 hour extraction time, 40°C temperature, and 7:1 dose rate reduced total uranium concentration in the extracted solids to 19 mg kg⁻¹.

Based on the findings from the bench-scale physical separation and chemical extraction testing, a combined approach was developed for final bench-scale testing before taking the process to pilot-scale. The ID-A and ID-B soil were subjected to an initial physical process followed by a chemical extraction process. Both soil were attrition scrubbed for 15 minutes using a 0.1 M sodium carbonate/sodium bicarbonate solution at a 2:1 dose rate (33 percent solids). At the end of this first part of the combined treatment process, the uranium concentration in the ID-A and ID-B soil were reduced to 341 and 241 mg kg⁻¹, respectively. This equated to a 31 and 46 percent reduction in the ID-A and ID-B soil respectively. These soil were then extracted for 30 minutes at 40°C with a 2 N sulfuric acid solution at a 7:1 dose rate (12.5 percent solids). The final concentration of uranium in the ID-A and ID-B treated soil solids following this sequential treatment process was 49 and 71 mg kg⁻¹, respectively. This equated to a 90 and 84 percent total reduction in the ID-A and ID-B soils, respectively. These operational parameters were then used to construct the processing conditions for operation of the soil washing pilot plant tests.

The initial configuration of the soil washing pilot plant was based on the fundamental designs of current soil washing systems within the United States. However, modifications to the design were implemented during construction of the pilot plant, resulting in a process configuration of the system specifically targeting FEMP soil. A 3000-square-foot, bi-level skid-mounted system was constructed to separate the soil into discrete-size fractions to facilitate separate treatment of each size fraction. Soil size cuts of the less than 19 millimeter (mm) feed soil were made at the trommel (4.75 mm), the screen deck (2 and 0.3 mm), and the centrifuge (approximately 0.02 mm).

The operation of the soil washing pilot plant was structured around a hybrid system incorporating physical separation processes with selected chemical extraction processes. The physical separation part of the system was directed at producing a selected soil size fraction from the feed soil that provided sufficient mass to warrant the use of an attrition scrubbing process. The attrition scrubbing part of the physical separation process incorporated a bisquential chemical extraction process which used multiple 0.1 M carbonate/ bicarbonate sequential extractions in the attrition scrubber followed by a 1 N sulfuric acid extraction process at 40°C to treat all soil solids greater than 0.02 mm. The less than 0.02 mm soil solids were solely extracted with 1 N H₂SO₄ at 40°C for 1 hour.

The soil washing pilot plant was operated in batch mode for a period of three months. Two batch runs (one 55-gallon drum of soil per batch run) of both the ID-A and ID-B soil were conducted during this pilot-scale testing. The two runs per soil were used to evaluate reproducibility of process operations and to provide some statistical reliability to the resulting data. Potentially, six basic process streams could have been generated during the operation of the soil washing system. Those streams included: (1) treated soil solids greater than 4.75 mm; (2) treated soil solids 0.3 to 4.75 mm (3) treated soil solids 0.02 to 0.3 mm; (4) treated soil solids less than 0.02 mm; (5) a filter cake (residue); and (6) spent carbonate extraction solution. Due to the operation of the soil washing system these primary process streams were slightly changed. The 0.3 to 4.75 mm soil solids coming off of the screen deck were combined with the 0.02 to 0.3 mm soil solids coming off of the centrifuge to form a single process stream. A centrifuge heel was created during system operations. The centrifuge heel was partially treated soil retained by the centrifuge during the batch-mode operation of the sys-

tem. Although this soil was not originally considered to be part of any primary process stream, it constituted such a significant amount of the initial soil mass and total uranium mass that it was used in the mass balancing of process operations. It should also be noted that although the centrifuge functioned very well as a dewatering device, it did not provide a particle-size separation at 0.02 mm.

Laboratory analysis by FERMCO, used to support mass balancing calculation for operation of the soil washing system, showed the initial average uranium concentration for the ID-A soil was 459 (SD=39.6) mg kg⁻¹ total uranium. The total uranium concentrations in the greater than 0.02-mm and less than 0.02 mm treated soil solids were 27 mg kg⁻¹ (SD=1.4) and 62.5 mg kg⁻¹ (SD=26.2), respectively. These two primary process streams, plus the greater than 4.75 mm gravel, accounted for an average of 74.3 percent (SD=4.4) of the initial total mass for the ID-A treated soil solids. This total mass of treated soil averaged 27 mg kg⁻¹ (SD=1.4). Residual total uranium mass remaining in the treated soil was approximately 10.3 percent (SD=0.4) of that contained in the feed soil. This equated to nearly a 90 percent reduction in total uranium mass for nearly 75 percent of the ID-A soil processed. Most of the uranium mass was either concentrated in the filter cake or remained in the spent carbonate extractant. The filter cake having a final total uranium concentration of approximately 637 mg kg⁻¹ (SD=209) contained 11.2 percent (SD=3.5) of the total uranium mass. Most of the uranium remained in the spent carbonate solution. This solution contained 71.5 percent (SD=16) of the total uranium mass. This solution also contained a significant amount of the initial soil mass, although an exact value could not be calculated. Much of this soil mass was the fine fraction of the soil separates that did not partition into the solid phase during centrifuga-

tion.

The initial average uranium concentration for the ID-B soil was 422 (SD=46.7) mg kg⁻¹ total uranium. The total uranium concentrations in the greater than 0.02-mm and less than 0.02 mm treated soil solids were 17 mg kg⁻¹ (SD=4.2) and 35.5 mg kg⁻¹ (SD=2.1), respectively. An additional quantity of effectively treated soil generated during the processing of the ID-B was the centrifuge heel. The centrifuge heel constituted nearly 31 percent of the initial soil mass with a final total uranium concentration of 60 mg kg⁻¹ (SD=19.1). These three primary process streams, plus the greater-than-4.75 mm gravel, accounted for an average of 78 percent (SD=10.7) of the initial total mass for the ID-B treated soil solids. This total mass of treated soil averaged 37 mg kg⁻¹ (SD=12.7). Residual total uranium mass remaining in the treated soil was approximately 6.7 percent (SD=2.5) of that contained in the feed soil. This equated to over a 90 percent reduction in total uranium mass for nearly 78 percent of the ID-B soil processed. Most of the uranium mass was either concentrated in the filter cake or remained in the spent carbonate extractant. The filter cake having a final total uranium concentration of approximately 3455 mg kg⁻¹ (SD=1281) contained 47.5 percent (SD=10.7) of the total uranium mass. A major portion of the uranium remained in the spent carbonate solution. This solution contained 23.5 percent (SD=11.8) of the total uranium mass. This solution also contained a significant amount of the initial soil mass, although an exact value could not be calculated. Much of this soil mass was the fine fraction of the soil separates that did not partition into the solid phase during centrifugation.

Off-site analyses by a contracted laboratory were also conducted in support of toxicity characteristic leaching procedure (TCLP) evaluation on the primary process streams

generated during the operation of the soil washing system. Total uranium concentration values for the initial soil and the primary process streams were consistently higher by off-site analysis as compared to on-site analysis. The average total uranium concentrations for the 0.02- to 4.75-mm process stream are 59 mg kg^{-1} (SD=4.2) and 75 mg kg^{-1} (SD=1.4) by the contracted laboratory, respectively, for the ID-A and ID-B soil. The average total uranium concentrations for the less-than-0.02-mm process stream were 158 mg kg^{-1} (SD=23.3) and 112 mg kg^{-1} (SD=2.1) by the contracted laboratory, respectively, for the ID-A and ID-B soil.

The TCLP results indicated that there is a reduction in the leachable quantity of uranium for the 0.02- to 4.75-mm and the less than 0.02-mm process streams, as compared to the initial soil. The initial feed soil showed TCLP values of 1206 and 11,398 pCi L^{-1} for the ID-A and ID-B soils, respectively. The 0.02- to 4.75-mm process stream was reduced to average TCLP values of 98 pCi L^{-1} (SD=50.9) and 267 pCi L^{-1} (SD=11.3) for the ID-A and ID-B soil, respectively. The less than 0.02-mm process stream was reduced to average TCLP values of 377 pCi L^{-1} (SD=358.5) and 712 pCi L^{-1} (SD=219.2) for the ID-A and ID-B soil, respectively.

2.2 Recommendations

A summary of the findings of this extensive testing has established a baseline understanding of the FEMP soil-contaminant matrix, as well as the potential effectiveness of soil washing on FEMP soil. The primary considerations when determining the effectiveness of soil washing for decontaminating FEMP soil must be premised with an understanding of the diversity of soil types, contaminant concentrations, and the resulting soil/contaminant matrices. The effectiveness of soil washing

with respect to a reduction in residual uranium mass and mobility, and this extrapolation to the concept of volume reduction, were evaluated based on the results from these extensive bench- and pilot-scale studies.

A hybrid soil washing system has evolved which emphasizes a sequential extraction process that incorporates a carbonate based reagent as a primary extractant followed by a sulfuric acid based secondary extraction process used on an as-needed basis. Using a conservative estimate for the potential effectiveness of a hybrid soil washing system, the data indicates that greater than 90 percent of the soil can be treated to a residual total uranium concentration of 100 mg kg^{-1} or less with a mobility of less than 1 mg L^{-1} total uranium established through TCLP testing.

3.0 TREATABILITY STUDY APPROACH

3.1 Study Objectives and Experimental Design

3.1.1 Study Objectives

Study objectives were established so that the performance of soil washing techniques could be evaluated on the basis of volume reduction, contaminant removal from individual soil fractions, and contaminant removal from the wash solutions. These performance objectives were used to determine if a particular series of physical/chemical processes could effectively and efficiently remove contaminants from soil. Only selected constituents found during the initial soil characterization in this study were targeted and followed through the treatability study.

The physical separation and chemical extraction tests were the focus of the bench-scale soil washing study. The test conditions which optimize the efficiency with which a radionuclide was extracted from the soil during these bench-scale studies were used to define the operational parameters for a pilot-scale soil washing system. The findings from the soil washing pilot-scale demonstration were used to evaluate the potential for soil washing to serve as a successful remedial technology for FEMP soil.

3.1.2 Soil Washing Experimental Design

Figure 3-1 shows the series of treatment stages that comprise the experimental design. This design for soil washing incorporated a tiered approach in determining (1) the binding association of radionuclides and other inorganic and organic chemical constituents within the soil matrix and (2) the physical separation and chemical extraction processes

necessary for soil washing and wash solution (spent extractant) recovery. This design incorporated the two parallel testing phases of physical separation and chemical extraction as part of the Stage I study, selectively separating soil into five individual soil size fractions (19.5 to 9.5 mm, 9.5 to 2 mm, 2 to 0.053 mm, 0.053 to 0.002 mm, and less than 0.002 mm).

The Remedy Screening-Stage I chemical extraction experiments were designed to examine gross effects on the less than 2 mm soil size fraction. The conditions were selected to yield favorable results (i.e., reagents that have a reasonable probability for success). The conditions chosen were high temperature (80°C), high reagent concentrations, and high dose rate (10:1 extraction solution to soil). The aggressive temperature and reagent

FIGURE 3-1. TREATMENT PHASES OF SOIL WASHING EXPERIMENTAL DESIGN FOR OPERABLE UNIT 5 SOILS.

conditions were selected to accelerate the rate of metal compound dissolution. The high dose (low percent solids) rate was used to minimize the effects of common ion effect and ionic strength on the dissolution of the desired material.

Initial screening tests conducted during Stage I studies were used to refine the Stage II approach for soil washing. The physical separation tests were used to identify the soil size fractions with which each type of contaminant (e.g., radionuclides and organic and inorganic compounds) was associated. Stage II Remedy Screening focused on these individual soil size fractions as part of the test matrix. The most effective washing solutions, determined during Stage I chemical extraction testing, were used for washing selected soil size fractions. The effect of extractant concentration and dose rate were to be determined.

Results from Stage II studies demonstrated the extraction reagents and concentrations that were most effective in removing radionuclides and other chemical constituents from selected soil size fractions. These results help establish the series of steps during physical separation and chemical extraction that are necessary to achieve a particular action level for contaminant removal. Also, the results from chemical extraction tests help determine the effectiveness of iterative chemical extractions in removing additional contaminants from soil and wash solutions or leachates. The Remedy Screening results were incorporated into the Remedy Selection advance phase testing and the pilot-scaled version of the soil washing treatment system.

3.2 Soils Used in the Soil Washing Treatability Study

3.2.1 Initial Selection of Soil

The Operable Unit 5 soil washing study requirements included the initial collection and characterization of soil used for treatability testing. Soil chosen for soil washing were initially selected from three locations that are considered to be representative of the contamination problem at the FEMP. The basic criteria for the type of soil selected, described in Section 6.0 of the TSWP, focuses on three soil with moderate to high uranium contamination. The selection of soil from one of these locations that also contain other inorganic and organic constituents allowed for soil washing treatability testing to address other specific contamination problems of soil at the FEMP.

Soil contaminated primarily with radionuclides (specifically uranium) were noted as "ID" soil. These soil were collected as part of the Uranium in Soil Integrated Demonstration (USID) program. Soil contaminated with radionuclides as well as other inorganic and organic chemicals was noted as "OU5" soil because it was unique to the Operable Unit 5 TSWP program. Specific reference to the three soil selected for use in this treatability study were given the following soil identifications: ID-A, ID-B, and OU5-A.

The ID-A soil was collected from the incinerator area. The source of uranium contamination in the surface soil in this area was incinerator emissions from burning low-level contaminated trash. The second soil was collected from the Plant 1 drum storage area and was identified as the ID-B soil. Contaminants in the surface soil of this area were thought to be introduced primarily by runoff from the drum storage pad. A complete characterization of the ID-A and ID-B soil is

provided in the report by Lee and Marsh (1992) and corresponds to the SP9/SP10 and SP3/SP4 soil, respectively. The locations of the two ID soil (ID-A and ID-B) selected for soil washing are illustrated in the TSWP.

The Operable Unit 5 (OU5-A) soil's uniqueness is due to the presence of COCs other than radionuclides. The source of contamination in Operable Unit 5-A soil is due to operations conducted at the maintenance building during production operation. The location of this soil is also given in the TSWP. Since much of the bench-scale testing conducted on the ID-A and ID-B soil had been performed before initiating testing on the OU5-A soil, the test program for the OU5-A soil was modified to test only the most effective extraction conditions. A description of the experimental design for the bench-scale testing of the OU5-A soil is contained in Section 3.3.4.

3.2.2 Initial Analysis and Characterization of Soil

Soil from each of the three locations were initially screened, homogenized, and placed into separate 55-gallon metal drums in accordance with Section 6.0 of the TSWP. Each area (approximately 6.2 by 7.7 m), was first prepared by removing all surface vegetation and the upper few centimeters of surface soil. The remaining upper 15 to 20 cm of soil was excavated and passed through a 19 mm screen to remove any cobbles, large gravel, and debris. The minus 19 mm soil was homogenized either in a large concrete mixer (ID-A and ID-B) or by shovel (OU5-A) and placed into 55 gallon plastic-lined metal drums. These resulting 15 and 16 drums for ID-A and ID-B soil were determined to be homogeneous with respect to particle size distribution and total uranium concentration (Kneff, et. al., 1992). The five drums of OU5-A soil collected were determined to have uniform distribution of total uranium and soil particle

distribution.

After the set of drums for each soil were determined to be homogeneous, a representative sample of soil from each drum was collected and composited and further homogenized using a stainless steel hand trowel. Physical and chemical characterization of all three soil (ID-A, ID-B, and OU 5-A) were conducted following collection and preceding treatability testing. A list of the parameters tested in this initial baseline characterization is presented in Table 3-1. This characterization was conducted in accordance with guidelines established in Section 3.0 and Section 6.0 of the TSWP. These analyses provided the initial baseline characterization of the soil for each location to be used in all subsequent treatability studies. The results of this initial characterization are provided in Section 4.1.

The concentration of other inorganic and organic COCs in the soil (termed HSL analytes in the TSWP) and the TCLP extract were determined for soil during the initial characterization and for the resulting treated soil following the Remedy Selection testing. This was considered necessary to address the criteria for targeted action cleanup levels as well as the potential applicable Resource Conservation and Recovery Act (RCRA) guidelines for returning treated soil to the site.

Soil to be used in bench-scale tests were removed from drums and transferred to five 5-gallon metal containers (approximately 23 kg of soil per container) and shipped to an IT Corporation laboratory in Oak Ridge, Tennessee for treatability testing. Because the soil contained in these drums was prepared in a manner representative of the bulk preparation of soil quantities in excess of 1000 kg, there was a need to further prepare the small quantities of soil sent to the laboratory before use in bench-scale tests.

TABLE 3-1**PARAMETERS FOR INITIAL BASELINE CHARACTERIZATION****Pesticides/PCBs**

4,4'-DDD
4,4'-DDE
4,4'-DDT
Aldrin
alpha-BHC
alpha-Chlordane
Aroclor 1016
Aroclor 1221
Aroclor 1232
Aroclor 1242
Aroclor 1248
Aroclor 1254
Aroclor 1260
beta-BHC
delta-BHC
Dieldrin
Endosulfan sulfate
Endosulfan-I
Endosulfan-II
Endrin
Endrin aldehyde
Endrin ketone
gamma-Chlordane
Heptachlor
Heptachlor epoxide
Methoxychlor
Toxaphene

Volatile Organics

1,1-Dichloroethane
1,1-Dichloroethene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane
1,2-Dichloroethane
1,2-Dichloroethene (total)
1,2-Dichloroethylene
1,2-Dichloropropane
2-Butanone
2-Hexanone
4-Methyl-2-pentanone
Acetone
Benzene
Bromodichloromethane
Bromoform
Bromomethane
Carbon disulfide

Carbon tetrachloride
Chlorobenzene
Chloroethane
Chloroform
Chloromethane
cis-1,3-Dichloropropene
Dibromochloromethane
Ethylbenzene
Methylene chloride
Styrene
Tetrachloroethene
Toluene
Total xylenes
trans-1,3-Dichloropropene

Semivolatile Organics

1,2-Dichlorobenzene
1,2,4-Trichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
2-Chloronaphthalene
2-Chlorophenol
2-Methylnaphthalene
2-Methylphenol
2-Nitroaniline
2-Nitrophenol
2,4-Dichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
2,6-Dinitrotoluene
3-Nitroaniline
3,3'-Dichlorobenzidine
4-Bromophenyl phenylether
4-Chloro-3-methylphenol
4-Chloraniline
4-Chlorophenyl-phenylether
4-Methylphenol
4-Nitroaniline
4-Nitrophenol
4,6-Dinitro-2-methylphenol
Acenaphthene
Acenaphthylene
Anthracene
Benzoic acid
Benzo(a)anthracene
Benzo(a)pyrene

TABLE 3-1**PARAMETERS FOR INITIAL BASELINE CHARACTERIZATION
(continued)**

Benzo(b)fluoranthene
Benzo(g,h)perylene
Benzo(k)fluoranthene
Benzyl alcohol
bis(2-Chloroethoxy)methane
bis(2-Chloroethyl)ether
bis(2-Chloroisopropyl)ether
bis(2-Ethylhexyl)phthalate
Butyl benzyl phthalate
Carbazole
Chrysene
Dibenzofuran
Dibenzo(a,h)anthracene
Diethylphthalate
Dimethylphthalate
Di-n-butyl phthalate
Di-n-octyl phthalate
Fluorene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Indeno(1,2,3-cd)pyrene
Isophorone
Naphthalene
Nitrobenzene
N-Nitroso-di-n-propylamine
N-Nitrosodiphenylamine
Pentachlorophenol
Phenanthrene
Phenol
Pyrerene

Inorganics

Aluminum (Al)
Antimony (Sb)
Arsenic (As)
Barium (Ba)
Beryllium (Be)
Boron (B)

Calcium (Ca)
Cadmium (Cd)
Chromium (Cr)
Cobalt (Co)
Copper (Cu)
Cyanide (Cn)
Lead (Pb)
Magnesium (Mg)
Manganese (Mn)
Mercury (Hg)
Molybdenum (Mo)
Potassium (K)
Nickel (Ni)
Selenium (Se)
Silicon (Si)
Silver (Ag)
Sodium (Na)
Thallium (Tl)
Vanadium (V)
Zinc (Zn)

Radionuclides

Cesium-137
Neptunium-237
Plutonium-238
Plutonium-239/240
Radium-224
Radium-226
Radium-228
Ruthenium-106
Strontium-90
Technetium-90
Thorium-228
Thorium-230
Thorium-232
Uranium-234
Uranium-235/236
Uranium-238
Gross alpha
Gross beta

3.2.3 Laboratory Preparation and Initial Analysis of Soil

The initial procedure for preparing soil received at the laboratory is illustrated in Figure 3-2. Approximately 50 kg (two 5-gallon containers each) of ID-A and ID-B soil were air dried for 48 hours and periodically stirred to ensure even drying. The soil was physically attenuated to break up large aggregates. Approximately 125 g batches of each soil were dry sieved through a stack of 9.5 and 2 mm Tyler stainless steel sieves for 30 minutes on a Ro-Tap shaker. The resulting three sample fractions (19 - 9.5 mm, 9.5 - 2 mm, and less than 2 mm) were then placed in separate plastic containers. Each container was then placed on a rotating jar mixer for 30 minutes and emptied into a 4.75 mm sample splitter. Each sample was split, recombined, and placed back into the plastic container to ensure that each fraction was homogeneous. This procedure ensured that the total amount

of each soil to be used for the initial analyses and during the various stages of testing had relatively the same textural composition and total uranium concentration. The remaining three 5-gallon containers (approximately 100 kg) of soil were retained as "whole soil."

The whole soil and the less than 2 mm size fraction were analyzed for homogeneity. Six aliquots from each soil were analyzed for total uranium by ion chromatography (IC). The less than 2 mm soil size fraction was used for the Stages I and II bench-scale tests. The whole soil (less than 19 mm) was used in Stage III testing. A grain size distribution analysis was conducted on the less than 2mm size fraction according to American Society for Testing and Materials (ASTM) D422-63 (ASTM 1991). The percentages of sand, silt, and clay were 23, 62 and 15 percent for ID-A soil and 27, 57 and 16 percent, respectively, for ID-B soil.

FIGURE 3-2. INITIAL PROCEDURE FOR PREPARING SOILS RECEIVED AT THE LABORATORY PRIOR TO INITIATING BENCH-SCALE TESTING.

3.2.3.1 Total Uranium Analysis by Ion Chromatography (IC)

Uranium analysis for solid and liquid samples were performed using a nitric acid digestion procedure followed by IC analysis using high performance liquid chromatography (HPLC). The HPLC incorporated a Perkin Elmer 204-S fluorescence detector [set at 515 nanometers (nm) emission wavelength] preceded by a Dionex HPLC-CG2 exchange resin. A 0.1 molar (M) phosphoric acid solution was used as the eluant. Soil to be analyzed were oven dried at 105°C for 12 hours before digestion. Soil digestion was performed on approximately 0.1 grams samples using 1 mL of concentrated nitric acid (HNO_3). Liquid digestion was performed on 1 mL aliquots of sample. Each sample was heated on a hot plate at 160°C until all moisture was gone, and then heated in a muffle furnace at 550°C for 15 minutes to remove nitrates or organics. This process was repeated until all residue was gone or no longer changed color. Digested samples were cooled and brought into solution with 1 mL of 25 percent HNO_3 and 19 mL of 0.2 percent phosphoric acid (H_3PO_4). Each solution was sonicated for 30 minutes at 59°C before analysis.

3.3 Bench-Scale Testing

3.3.1 Stage I: Physical Separation Tests

3.3.1.1 Test Objectives

The initial objective of physical separation testing was to characterize the soil/contaminant matrix relative to particle size distribution and the level of uranium (the radiological contaminant) associated with individual soil size fractions. As part of this initial stage in the soil washing bench-scale treatability study, basic physical separation techniques were tested to derive the level and tenacity of the

soil/contaminant association. A second objective was to evaluate chemical dispersants and their effectiveness in aggregate dispersion and uranium extraction. The third and final objective was to test a combination of physical and chemical treatments in order to define the best dispersant and physical separation parameters for removing uranium from the two test soil.

3.3.1.2 Chemical Dispersant/Extractant Tests

ID-A and ID-B Soil

Four dispersing reagents and potable water were tested to determine their effectiveness in: (1) deflocculating soil aggregates into single grain separates and (2) removing uranium from the resulting soil fractions. The dispersants were 1 millimolar (mM) solutions of sodium carbonate (Na_2CO_3), sodium bicarbonate (NaHCO_3), sodium hydroxide (NaOH) and a sodium citrate/bicarbonate/dithionite (CBD) mixture (Lee and Marsh 1992). Potable water was used for making all dispersant solutions.

The less than 2 mm size fraction of ID-A and ID-B soil (250-g samples) were reacted in a 2 liter (L) flask with 500 mL of a 1 mM solution of each dispersant. Each sample was agitated at low speed on a shaker table for 30 minutes before sieving. The slurry was transferred to a stack of Tyler stainless steel sieves (9.5 mm, 2 mm, and 0.053 mm). The sieves were completely sealed and the slurry was Ro-Taped for 1 hour. The soil on each sieve was collected and dried at 105°C and analyzed for total uranium.

The dispersing solution and the less than 0.053 mm soil slurry were collected. This slurry was subjected to a modified version of the M.L. Jackson procedure (Jackson 1975) using centrifugation for separating silt (0.002 - 0.053 mm) from clay (less than 0.002 mm) and clay from the solution. Sufficient dispersing solution was initially added to the less

than 53 μm slurry to make a final 1800-mL volume for each dispersant/soil slurry. While being agitated on a stir plate, 100-mL aliquots of the slurry and 100-mL of dispersing solution were placed into 250-mL centrifuge tubes, shaken, and centrifuged at 800 revolutions per minute (rpm) for seven minutes. The time and speed were calculated from Stokes law in integrated form, which yields time needed for sedimentation under centrifugal acceleration for a given particle diameter.

The supernatant, dispersant solution, and less than 0.002 mm soil were decanted into a 2-L beaker following centrifugation. The solids were resuspended by adding more dispersing solution, shaken, and centrifuged. This process continued until the supernatant appeared clear (approximately 5-6 times). The final 0.002-0.053 mm soil fraction remaining in the centrifuge tube following this procedure was slurried with potable water and dried at 105°C. The combined supernatants (less than 0.002 mm soil slurry) were centrifuged at 3000 rpm for 60 minutes to separate the final

soil size fraction from the dispersing solution. The resulting two soil size fractions (less than 0.002 mm and 0.002-0.053 mm) were analyzed for total uranium.

3.3.1.3 Attrition Scrubbing Tests

The ID-A and ID-B soil were subject to attrition scrubbing testing using a modified Hamilton Beach mixer (Figure 3-3). The 13,000 rpm mixer was modified by replacing the single agitator propeller with two oppositely pitched propellers placed approximately 5 to 7 cm apart on the mixer shaft. During operation, the top blade forces sample down and the bottom blade forces sample up, causing an attriting action of the soil particles with each other.

Three dispersant solution and potable water were tested on both soil to determine their effectiveness in removing uranium from the less than 2-mm soil size fraction. A $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ solution, an ammonium carbonate/

FIGURE 3-3. THE PROCEDURE FOR ATTRITION SCRUBBING TESTS.

ammonium bicarbonate solution ($(\text{NH}_4)_2\text{CO}_3/(\text{NH}_4)\text{HCO}_3$), a sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$), and potable water were used in the attrition scrubbing tests. The ammonium and sodium carbonate solutions were tested at a 3:1 ratio of carbonate to bicarbonate.

All three dispersant solutions were tested on both soil at three concentrations (0.1 M, 0.25 M, and 0.5 M) and three attrition scrubbing times (5, 15, and 30 minutes). A 1:2 ratio of air-dry soil to dispersant solution was used. The pH of the slurry was measured at the completion of the attrition scrubbing time. The soil slurry was transferred onto a 53 μm sieve with lid and collection pan, completely sealed, and shaken for 30 minutes on the Ro-Tap shaker. The greater than 53 μm fraction was then washed on the sieve with potable water and dried at 90°C. The less than 53 μm soil slurry was transferred to 200 ml centrifuge tubes and centrifuged for 1 hour at 2500 rpm. This centrifugation separated all the solids greater than 0.12 μm from the liquid. The solids were weighed and analyzed for total uranium.

3.3.2 Stage I: Chemical Extraction Tests

3.3.2.1 Test Objectives

The chemical extraction tests were designed in phases to selectively and sequentially investigate certain aspects of chemical extraction. Successful results from each phase of testing were transferred to subsequent phases of testing to further refine the use of chemicals for extraction of uranium from the soil. The initial objective of the first phase of the chemical extraction tests was to evaluate the effectiveness of various types of acids, bases, chelants, and salts in removing uranium from each soil. The second objective, Phase II testing, was to select the most successful chemical reagents from Phase I and evaluate the effect of reagent concentration on chemi-

cal extraction. The final objective, Phase III testing, was to evaluate the effects of temperature, reaction time, and dose rate (extracting solution to soil ratio), using the lowest successful concentrations of extraction reagents from Phase II.

3.3.2.2 Phase I: Initial Screening of Chemical Extractants

Twelve chemical reagents were tested on the ID-A and ID-B soil in this phase of the study. This stage of testing is illustrated in Figure 3-4. The chemicals tested (shown in Table 3-2) ranged from concentrated inorganic acids to salt solutions. The chemical extractants and corresponding extracting solution concentrations included: 1:1 aqueous concentrations of concentrated sulfuric, hydrochloric, nitric, and

FIGURE 3-4. PHASE I OF REMEDY SCREENING TESTS FOR CHEMICAL EXTRACTION OF ID SOILS.

TABLE 3-2**TEST PROGRAM FOR ID SOILS EXTRACTANT SCREENING**

Extractants	Concentration	Dose Rate	Temperature (°C)
<u>Acids/Bases/Salts</u>			
H ₂ SO ₄	1:1	10:1	80
HCl	1:1	10:1	80
HNO ₃	1:1	10:1	80
H ₃ PO ₄	1:1	10:1	80
Na ₂ CO ₃	60/20 (g/L)	10:1	80
NaOH	4.0 N	10:1	80
(NH ₄) ₂ CO ₃ /(NH ₄)HCO ₃	60/20 (g/L)	10:1	80
NaCl	15%	10:1	80
KCl	15%	10:1	80
<u>Chelants</u>			
EDTA			
pH 6.00	0.5 M	10:1	80
pH 8.00	0.5 M	10:1	80
pH 10.00	0.5 M	10:1	80
NS1	1:10	10:1	80
Citrikleen	1:10	10:1	80

phosphoric acids; 60 g/20 g per liter concentrations of sodium carbonate/sodium bicarbonate and ammonium carbonate/ammonium bicarbonate; 4.0 N sodium hydroxide; 15 percent sodium chloride and 15 percent potassium chloride; 0.5 M ethylene diamine triacetic acid (EDTA) at three pH values (6, 8, and 10); 10 percent NS1 (a proprietary extractant); and 10 percent Citrikleen™. The extraction equipment used in the study consisted of six 1000 mL Pyrex reaction kettles with mechanical stirring (approximately 150 rpm) provided by a modified Phipps & Bird six-paddle stirrer (Figure 3-5). All stirrers had rods and Teflon™ paddles. The kettles were heated by a heating mantle which was electrically regulated by a thermocouple and controller. Vapor losses from the kettles were minimized by placing a condenser and a Teflon gasket between the top and bottom

sections of the kettles. Vacuum filtration was performed using a Spectrum Mesh Filtration unit with a 20 to 25 micron glass fiber filter.

Approximately 50-g aliquots of homogenized soil were reacted with each extractant in a 10:1 (wt:wt) ratio of extracting solution to soil. The soil and extractant solution were reacted in the heated kettles for 4 hours at 80°C. At the conclusion of the reaction time, each soil slurry was filtered to separate the spent extracting solution from the soil solids. The spent extractant was collected for analysis. The soil solids on the filter (filter cake) were reslurried with 200 mL of deionized water and filtered. This was to reduce the residual extractant concentration and remove additional uranium remaining in the filter cake. The rinsate solution and extracted soil solids were collected separately for analysis.

FIGURE 3-5. MODIFIED PHIPPS & BIRD STIR REACTOR.

The extracted solids, extractant solution, and rinse water were analyzed for uranium by IC. The efficacy of each extractant was evaluated based on the final concentration of uranium in the extracted soil solids, and the calculated percent removal of uranium during the extraction process. The percentage of uranium removed was calculated by summation of solids, spent extractant, and rinse water. All tests were run as single replications and no statistical analysis was performed.

3.3.2.3 Phase II: Screening of Selected Extractants

Phase II testing (see Figure 3-6) incorporated the most effective chemical extractants from Phase I testing. Three inorganic acids, sulfuric, nitric, and hydrochloric, were selected to

further evaluate their effectiveness in removing total uranium from the ID-A and ID-B soil. Each extractant was tested at five concentrations to determine the lowest concentration of extractant that could be used without significantly diminishing the amount of total uranium removed from the extracted solids.

Sulfuric acid was tested at 0.2, 1, 2, 12 and 18 (1:1) normal (N); nitric acid at 0.1, 0.5, 1, 5.3, and 8 (1:1) N; and hydrochloric acid at 0.1, 0.5, 1, 4, 6 (1:1) N. The extraction time (4 hours), temperature (80°C), and dose rate (10:1 wt/wt) were kept the same as in Phase I testing. The extraction apparatus and methodology were the same as used in Phase I testing. All tests were run as single replications and no statistical analysis was performed.

FIGURE 3-6. PHASE II OF REMEDY SCREENING TESTS FOR CHEMICAL EXTRACTION OF ID SOIL.

3.3.2.4 Phase III: Time, Temperature, and Concentration Study

Two of the inorganic acids tested in Phase II were carried over to Phase III and tested on both the ID-A and the ID-B soil. Phase III testing was designed to evaluate the effects of extractant concentration, temperature, dose rate, and extraction time on the amount of total uranium removed from the extracted solids. Sulfuric acid and nitric acid were tested at 1 and 2 N concentrations. Each concentration of acid was tested at 4:1 and 7:1 dose rates (20 and 12.5 percent solids respectively), two extraction times (0.5 and 2 hours) and two temperatures [ambient (approximately 20°C) and 40°C]. The test design consisted of a four by four matrix incorporating the two levels of each of the four variables. All tests were run as single replications and no statistical analysis was performed.

3.3.3 Stage II: Physical Separation and Chemical Extraction Tests

3.3.3.1 Test Objectives

The objective of this stage of testing was to combine the most favorable conditions from physical separation and chemical extraction testing into a sequential process and test its efficacy in removing uranium from soil. The testing of the combined process (physical separation and chemical extraction) was performed on dried "as received" soil. Since this stage of testing incorporated the use of a Denver Equipment Company (DECO) attrition mill (see Figure 3-7), an initial test was conducted to compare the use of a Hamilton Beach mixer with a DECO attrition mill and the effects of the two different mixing speeds on uranium concentration of both the ID-A and ID-B soil.

FIGURE 3-7. DENVER EQUIPMENT COMPANY ATTRITION SCRUBBER.

3.3.3.2 Experimental Design Comparison Test

ID-A and ID-B soil were attrition scrubbed in both a Hamilton Beach mixer and a DECO attrition mill. The Hamilton Beach and the DECO mixers operate at 13,000 and 900 rpm, respectively. A 2:1 slurry was made by adding 200 g of dry less than 2 mm soil to 400 g 0.25 M $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ solution.

Each soil slurry was mixed for 5, 15, and 30 minutes. The slurry was transferred to a Ro-Tap shaker to separate out the greater than 53 μm soil fraction. The less than 0.053 mm soil slurry was transferred to centrifuge tubes for phase separation. The greater than and less than 0.053 mm size fractions and the spent carbonate extractant were analyzed for total uranium.

FIGURE 3-8. STAGE II OF REMEDY SCREENING TESTS FOR COMBINED PHYSICAL SEPARATION AND CHEMICAL EXTRACTION OF ID SOILS.

Combined Test

The combined physical separation and chemical extraction test is illustrated in Figure 3-8. Approximately 200 grams of "as received"

ID-A and ID-B soil were attrition scrubbed with 400 grams of 0.1 M Na₂CO₃/NaHCO₃ for 15 minutes using the DECO attrition mill. The soil slurry was dewatered by centrifugation at 2500 rpm for 88 minutes. The liquid was decanted and the soil sampled and analyzed for total percent water, uranium by IC, and metals by ICP. The liquid and soil were analyzed for total uranium and metals. The remaining soil solids were divided into two approximately equal soil masses and subjected to chemical extraction. All attrition scrubbing tests were conducted in duplicate.

Each soil sample was extracted at a 4:1 and 7:1 extractant-to-soil ratio dose rate with 1 N sulfuric acid at 40°C for 30 minutes. Following extraction, the samples were centrifuged at 2500 rpm for 88 minutes. The resulting liquid was decanted off and the soil was dried at 100°C. The liquid and soil were analyzed for total uranium and ICP metals (Table 3-3).

TABLE 3-3

ICP METALS ANALYZED DURING COMBINED PHYSICAL SEPARATION AND CHEMICAL EXTRACTION TESTING

Aluminum (Al)
Antimony (Sb)
Arsenic (As)
Boron (B)
Barium (Ba)
Beryllium (Be)
Calcium (Ca)
Cadmium (Cd)

Copper (Cu)
Iron (Fe)
Lead (Pb)
Magnesium (Mg)
Manganese (Mn)
Molybdenum (Mo)
Nickel (Ni)
Potassium (K)

Silver (Ag)
Sodium (Na)
Thorium (Th)
Thallium (Tl)
Uranium (U)
Vanadium (V)
Zinc (Zn)

3.4 Pilot-Scale Testing

3.4.1 CRU5 Soil Washing Demonstration Tests

3.4.1.1 Test Objectives

The intent of this Remedy Selection stage of testing was to demonstrate and evaluate the effectiveness of a soil washing process on two FEMP soil. The soil washing pilot plant's design and operation was based on findings from initial soil characterization efforts as well as extensive bench-scale testing. By demonstrating bench-scale findings on a pilot-scale system, this CERCLA/RCRA Unit 5 (CRU5) coordinated demonstration could be used to evaluate the performance effectiveness and cost effectiveness of a pilot-scale soil washing system for remediating FEMP soil.

3.4.1.2 Equipment Used in the Soil Washing Pilot Plant

The soil washing pilot plant was designed and constructed of standard processing equipment common to the mining industry. Equipment used in the soil washing system consisted of a conveyor, trommel, vibrating screen deck, attrition scrubber, centrifuge, filter press, holding tanks, and reactor vessels. The following is a brief description of each piece of equipment.

Drum Handling Station and Conveyor - The drum handling station consisted of a drum handler and hoist to raise, lower, and move drums. Calibrated scales were used to record the weight of each drum, before and after the soil was loaded onto the conveyor. The conveyor transported contaminated soil from the drum emptying area to the trommel screen. The conveyor was rated at a maximum capacity of 160 tons per hour (tph) with an incline of approximately 15 degrees.

Trommel Screen with High Pressure Sprayer

The trommel screen was a rotating drum screen with 4.75 mm screen openings. Lifter bars were used to assist in breaking down soil aggregates. A spray bar was oriented along the inside top of the trommel to distribute the high pressure water [1,000 pounds per square inch (psi)] along the entire horizontal length of the rotating drum.

Vibrating Screen Deck - The modified Best duel screen deck used vibrational and oscillating forces to separate soil by particle size. The bi-level deck consisted of a top 2 mm (10 mesh) stainless steel screen and a bottom 0.3 mm (50 mesh) stainless steel screen. The deck was tilted 0.25 inches from front to back along the 60-in length.

Centrifuge - The Hysep Decanter MD43 horizontal duel-scroll centrifuge generated a maximum of 3000 gravity (g) force. The centrifuge, consisting primarily of a bowl and scroll, used differential speeds between the bowl and scroll to separate liquids from solids.

Attrition Scrubber - The attrition scrubber unit consisted of two 0.5 cubic foot cells in series. Each cell was equipped with opposed axial flow impellers (one at 100 percent pitch and the other at 150 percent pitch), which ran at low rpm. This differential in pitch resulted in a high impact zone between the propellers, creating an intense multiple grain-to-grain contact. The low rpm minimized any shearing action by the impellers on the soil particles.

Filter Press - The SP JWI plate and frame filter press had 6 cubic feet total volume capacity with a 3000 psi hydraulic closing mechanism. The unit consisted of twenty 0.3 cubic-foot chambers with polypropylene filter cloth-lined plates.

Processing Tanks - Most processing tanks were polyvinyl chloride (PVC) cone-bottom

tanks with 0.25 inch thick fiberglass reinforced plastic (FRP) encasement. Tanks ranged in capacity from 50 to 500 gallons.

Chemical Extraction Reactor Vessel - The chemical extraction vessel was a glass-lined, closed-top, jacketed reactor. The working capacity was 500 gallons with a gross capacity of 578 gallons. The jacket capacity was 110 gallons with a heating area of 80 square feet. The reactor was equipped with a three retreat agitator.

Process Pumps

The majority of transfer operations used Wilden air driven diaphragm pumps. Aluminum pumps with Buna N diaphragms were used for the physical treatment; Kynar® pumps with Teflon® diaphragms were used for the chemical treatment. Three different models, the M-4, the M-8, and the M-15, were available in aluminum, while only the M-4 and M-8 were manufactured from Kynar®. Additional pumps used in the system were the Goulds model NPE centrifugal pump, a Pacer centrifugal pump, and a Masterflex B/T peristaltic pump.

Agitators/Mixers

Nettco mixers were used for all of the 500-gallon tanks except for the reactor vessel. The mixers were equipped with 1/2-hp motors, 1 inch diameter shafts, and three-blade propellers (10.5 inches in diameter). Propeller speed was 350 rpm. All tanks smaller than 500 gallons were equipped with portable Lightnin mixers. These mixers are gear-driven models having impeller diameters of 11.2 inches.

3.4.1.3 Chemicals Used in the Soil Washing Pilot Plant

Aqueous reagent formulations of sulfuric acid and sodium carbonate/sodium bicarbonate were used in the washing solutions for the extraction of uranium from the different soil

size fractions. Concentrated sulfuric acid was metered into the extraction vessel containing a soil-water slurry to achieve a 1 N acid extraction solution. Sodium carbonate/sodium bicarbonate was added in powder form to the processing tank during the attrition scrubbing part of the soil washing process. Twenty percent sodium hydroxide was added to spent sulfuric acid solutions to precipitate metals from the spent extraction solution. A Betz 1147L polymer was used at a 0.5 percent concentration to aid phase separation during the centrifugation of the soil/acid solution following the chemical extraction process.

3.4.1.4 Soil Washing System Design and Operation

The soil washing system design, a collaborative effort between IT Corporation and FERMCO, is illustrated in Figure 3-9. The system incorporated a combination of physical separation and chemical extraction processes for removing contaminants (primarily uranium) from FEMP soil. The physical/chemical treatment processes initially separated the soil into different particle-size fractions and then used physicochemical extraction techniques to remove contaminants from each size fraction.

The process flow for the system was designed to treat soil that had been prescreened through a 19 mm screen. A representative process flow diagram (PFD) for the soil washing pilot plant is shown in Figures 3-10 and 3-11. The system was operated in batch mode during pilot-scale testing. A single 55-gallon drum of soil was processed through the system for each run of the entire process.

Soil was introduced into the system by transferring soil by hand from the drum onto the conveyor. This soil was conveyed to a trommel where high pressure water was used to break down soil aggregates in individual

FIGURE 3-9. 3-DIMENSIONAL COMPUTER MODEL OF THE SOIL WASHING PILOT PLANT - 4 VIEWS

NOTES:

1. ALL MATERIAL FROM THIS OPERATION CONSUMED BY SAMPLE
2. APPROXIMATELY ONE CUBIC FOOT OF MATERIAL ACCUMULATES IN ATTRITION SCRUBBER AT THIS OPERATION, NOT REFLECTED IN TOTAL MASS FOR SUBSEQUENT STREAM.
3. ATTRITION SCRUBBER EMPTIED AFTER THIS OPERATION.

FIGURE 3-10. A PROCESS FLOW DIAGRAM FOR THE PHYSICAL SEPARATION OPERATIONS IN THE SOIL WASHING PILOT PLANT.

FIGURE 3-11. A PROCESS FLOW DIAGRAM FOR THE CHEMICAL EXTRACTION OPERATIONS IN THE SOIL WASHING PILOT PLANT.

discrete gravel and soil particles and to remove clay particles from the surface of larger particles. The high pressure sprayer was maintained at a maximum pressure of 1,000 psi and 4 gallons per minute (gpm) flow rate. The retention time in the trommel, considered critical for proper aggregate dispersion and clay removal from the larger particles, was controlled by the rotational speed and angle of the trommel. Optimum conditions were 4 rpm at an angle between 1 and 2 degrees decline. High pressure water injected into the trommel was directed at the soil as it rolled up on the inner rotating screen and out of the slurry on the bottom of the trommel. This maximized direct contact of the spray with soil aggregates and minimized any buffering effect due to the pooling of water on the bottom of the trommel. The oversize gravel fraction (greater than 4.75 mm), predetermined to constitute less than 5 percent of the initial soil mass, was discharged as the first process stream.

The undersize fraction passed through the trommel screen and was collected in a modified covered bowl pump, where it was transferred via a Wilden Kynar® M-8 diaphragm pump and 2 inch polypropylene SuperVac vacuum hoses as a slurry to the vibrating screen deck. Since the vibrating screen deck was not completely covered, the slurry was pumped to the screen deck at the slowest rate possible to avoid any splashes or spills. The air supplied (120 psi regulated) to the diaphragm pump was maintained below 20 psi.

The vibrating screen deck was designed with two decks of screens to produce three size fractions. The first 2 mm screen (10 mesh) retained the 4.75 to 2 mm soil size fraction. The second 0.3 mm screen (50 mesh) retained the 2 to 0.3 mm soil size fraction. The less than 0.3 mm slurry was collected below in a 500 gallon tank. Although the screens were removable and a different set of cuts could

have been made, the selected cuts were considered optimum to enhance process operations. The 2 mm screen kept the lower 0.3 mm screen from blinding during the screening process, while the 0.3 mm cut was determined to be the maximum particle size obtainable during operation and also provided ware protection to the centrifuge from coarse particles. The deck was tilted 0.25 inches from front to back to allow the material to flow gravimetrically off the screen. This angle also provided enough retention time for effective separation of the material. This resulting soil fraction (4.75 to 0.3 mm) was collected and later combined with the solids from the centrifuge process step before processing through the attrition scrubber.

The less than 0.3 mm soil slurry was pumped to the Hysep Decanter MD43 centrifuge at an about 5 gpm flow rate where the soil-water slurry was subjected to phase separation. The centrifuge provided continuous separation in a horizontal bowl which contained a double decanter system. From the center feed-pipe, the slurry was fed into the inner decanter where the initial separation and thickening of the slurry took place. Thickened slurry was then passed to the outer decanter where liquid and solids were separated. Solids scrolled out through the dry solids outlet and the overflow flowed back to its own outlet. During pilot plant operation, the centrifuge was configured to provide a bowl speed of 2041 rpm and a scroll speed of 2056 rpm at a differential of 15 rpm with 1100g force.

The objective of this design was to operate the centrifuge to obtain a 0.020 mm soil particle size cut. Two process streams were generated during this part of the process. The solids (estimated to be approximately 65 percent solids) from the centrifuge were estimated to contain soil particles in the 0.02 to 0.3 mm size range, were transferred to the attrition scrubbing part of the process. The centrate

[soil-water slurry (ca. 5 to 10 percent solids)] resulting from the centrifugation process was estimated to contain the less than 0.02 mm soil particles and was pumped directly to the chemical extraction reaction vessel for acid extraction.

A 0.02 mm particle size separation using the centrifuge was a critical part of the design. First, soil separates greater than 0.02 mm are silt and sand particles. The attrition scrubber operates optimally on particles in the sand fraction (greater than 0.05 mm), while clay particles (less than 0.002 mm) have a tendency to buffer the attriting action. The silt particles (0.002 to 0.05 mm) which fall between the clay and sand particles in size but physically resemble the sand particles since they don't have a lattice structure like clays, were thought to behave like sand particles with respect to attrition scrubbing. Second, since uranium contamination was characterized to partially exist as oxide coatings on the coarser particles, attrition scrubbing with carbonate additives was considered to be the optimum method for surface removal. Third, since less than 15 percent of the soil solids were greater than 0.3 mm and in order to justify an attrition scrubbing step in the soil washing process, a more significant mass of soil needed to be directed to the attrition scrubber. By producing a particle size fraction greater than 0.02 mm, approximately 50 percent of the soil could be directed to the attrition scrubber. Fourth, since the attrition scrubber operates optimally in the range of 60 to 70 percent solids, the greater than 0.02 mm soil size fraction produced by the centrifuge was dewatered to approximately this range during phase separation.

The 0.02 to 0.3 mm soil from the centrifuge was combined with the 0.3 to 4.75 mm soil from the screen deck. This 0.02 to 4.75 mm size fraction, consisting of about 50 to 70 percent solids, was fed to the attrition scrub-

ber. The solids were loaded into a feed box at the top of the first cell, flowed from the bottom of the first cell to the second cell, and exited at the top of the second cell through a flanged opening. Soil was fed in batches to allow a 15 minute retention time per cell. The solids overflowed into a 500-gallon tank. This first attrition scrubbing cycle did not contain sodium carbonate/bicarbonate. Once through the attrition scrubber, the solids were repulped in the 500-gal collection tank using a 0.1 M sodium carbonate/bicarbonate solution. This repulping process with water facilitated slurry pumping and sodium carbonate/bicarbonate addition. This slurry was dewatered using the combined screen deck and centrifuge. This soil processing combination utilizing the screen deck, centrifuging, and attrition scrubber was repeated three times during each run. Sodium carbonate/sodium bicarbonate was added during the first and second repulping cycles. These solids were repulped with water following the third attrition scrubbing. This final soil slurry was transferred to the extraction vessel and reacted with concentrated sulfuric acid in a 1 N solution for one hour at 40°C. Although some residual sodium carbonate/bicarbonate remained in the soil slurry before acid extraction, sufficient concentrated sulfuric acid was metered into the extraction vessel (based on an estimate of the total volume of slurry in the extraction vessel) to achieve a 1 N solution.

Following the final extraction process step for this 0.02 to 4.75 mm size fraction, the slurry was transferred to the centrifuge for a final dewatering step. Polymer was added as the soil slurry entered the centrifuge to enhance flocculation of the suspended particles and aid in phase (solid-liquid) separation. Polymer flow rates varied from approximately 0.1 to 0.5 gpm during the 5 gpm extracted soil slurry flow rate.

The centrate (containing the less than 0.02

mm soil size fraction) initially coming off the centrifuge was pumped directly to the reactor vessel. Concentrated sulfuric acid was metered into the reactor vessel to achieve a 1 N H_2SO_4 solution. The slurry was reacted for one hour at 40°C. This process stream was estimated to contain approximately 30 percent of the initial soil mass. Following the extraction step, the slurry was pumped through the centrifuge for phase separation. Polymer was metered into the slurry as it entered the centrifuge to promote flocculation and aid solids separation. The solids generated during this phase separation were repulped with water as a rinse cycle and processed through the centrifuge again for phase separation. These solids (less than 0.02 mm soil particles) were collected as a final treated soil process stream. The centrate resulting from both centrifugation steps was collected and pumped to a precipitation reaction vessel.

The spent acid extractant and spent rinse water were precipitated with a 20 percent NaOH solution. The NaOH solution was metered into the precipitation vessel so that the precipitation process was performed in three stages: at pH values of 4.5, 7.5, and 9.5. Continuous agitation was conducted during the NaOH addition. The final solution was allowed to stand for 24 hours. The supernatant was pumped from the tank and collected, while the solids were pumped to the filter press and dewatered. The filtrate and filter cake were collected.

3.4.1.5 Analytical Support

Analytical support was carried out on two levels during the operation of the soil washing pilot plant. In-house analyses were conducted by the FERMCO laboratory and outside analyses were conducted by contracted laboratories.

In-house analyses were directed at tracking soil mass and total uranium (the target analyte) throughout the soil washing process operation. This soil mass and uranium mass tracking supported the detailed description of process operations by mass balancing each run of soil through the soil washing pilot plant. Total uranium was determined by the BrPADAP method. In addition to total uranium, pH, percent solids, and percent moisture were determined during many of the process operations.

Each run of soil through the soil washing system generated six primary process streams. These process streams included four processed (treated) soil, solids, a residue, and spent extractant solution. These primary process streams were analyzed by a Contract Laboratory Program laboratory to provide specified analytical support level (ASL) analyses of final process streams for all COCs (Table 3-1). Since no VOCs or SVOCs were determined in the initial characterization, only radionuclides, inorganic analytes and PCBs were analyzed for in each of the final process streams.

3.5 Additional Soil Washing Process Testing for Other COCs

3.5.1 Test Objectives

The intent of this additional remedy selection stage of testing was to demonstrate and evaluate the effectiveness of a bench-scale simulated soil washing process on additional FEMP soil. The OU5-A soil had been the only soil of the three soil initially characterized to contain other COCs besides uranium. However, the OU5-A soil contained minimal quantities of a limited number of COCs; Therefore, an additional nine soil were collected to test in bench-scale soil washing process.

A simulated soil washing process was designed to provide a combination of residence time and reactor conditions that would be expected in the actual soil washing process as described in the Conceptual Design Report for CRU5. The three original soil and the nine additional soil (AS) tested were selected to test the soil washing process on a variety of soil containing a range in contaminants of concern (COCs) at the FEMP.

3.5.2 Experimental Design and Procedures

3.5.2.1 Location of Additional Soil (AS) for Testing

Nine additional locations within the FEMP were determined, based on RI data, to have soil containing other COCs. The following is a list of the soil and the areas within the FEMP from which the soil were collected:

- AS-1 - Plant 9 (archive sample)
- AS-2 - Plant 2/3 (archive sample)
- AS-3 - Plant 6 (archive sample)
- AS-4 - Pilot Plant
- AS-5 - Graphite Furnace
- AS-6 - Paddy's Run
- AS-7 - KC-2 Warehouse
- AS-8 - Decontamination and Demolition (D&D) Facility
- AS-9 - Building 77/79

3.5.2.2 Preparation and Initial Characterization of Additional Nine Soil

The AS-1, AS-2, and AS-3 soil were soil that had been collected during RI sampling and archived in glass jars sealed with Teflon™ lined caps. Soil for each of the AS samples

were combined by location and air dried for approximately 24 h. The soil were passed through a 2 mm screen. The greater than 2 mm aggregates were broken down using a mortar and pestle and passed through a 2 mm screen. All less than 2 mm soil was combined and homogenized by the quartering method. A single aliquot of the homogenized less than 2 mm soil was sent to a contracted laboratory for initial characterization which included analysis for radionuclides, inorganics (metals), SVOCs, VOCs, PCBs, and pesticides.

The AS-4, AS-5, AS-6, AS-7, AS-8, and AS-9 soil were specifically collected from their respective location (Section 3.5.2.1) for this additional bench-scale treatability testing. Exact areas within the defined locations were determined according to the procedure described in Section 6.0 of the TSWP. Two-foot square areas were excavated to a depth of six inches. The soil was passed through a 4.75 mm screen and placed into 5 gallon metal buckets. These soil were transferred to the laboratory, air dried, passed through a 2 mm screen, and homogenized. The greater than 2 mm aggregates were broken down using a mortar and pestle and passed through a 2 mm screen. A single aliquot of the homogenized less than 2 mm soil was sent to a contracted laboratory for initial characterization which included analysis for radionuclides, inorganics (metals), SVOCs, VOCs, PCBs, and pesticides.

Based on the initial characterization, certain soil were selected for additional testing. These soil were selected based on two characteristics. Soil that had total uranium concentrations different than the ID-A, ID-B and OU5-A soil were selected to increase of range in uranium concentrations over which the soil washing process could be evaluated as to its effectiveness in removing uranium. Soil were also selected if additional COCs were detected so as to evaluate the effectiveness of the

soil washing process on soil contaminated with other constituents besides uranium. The three additional soil were selected were AS-3, AS-4 and AS-7. The Plant 6 soil (AS-3) was selected because of the high levels of total uranium. The pilot plant soil (AS-4) was selected due to the presence of other COC, including radionuclides and metals. The KC-2 Warehouse soil (AS-7) was selected because of the low concentration of total uranium.

3.5.2.3 Simulated Soil Washing System Test

The bench-scale soil washing test incorporated a test procedure that was modeled after the preliminary CRU5 CDR flow diagram of the proposed soil washing system. This mock-run of the soil washing process was designed around selected operational parameters that simulated processing condition, e.g., temperature, soil to extractant ratio, staging time during processing operations, and rinse cycles.

Sodium Carbonate/Sodium Bicarbonate System

During the testing of the carbonate simulated soil washing system, 600 g of each soil was combined with 1200 mL of a 0.5 M sodium carbonate/sodium bicarbonate solution in a 2.2 L Teflon bottle. The soil-extractant slurry was shaken for approximately 1 min, and placed into a constant-temperature water bath at 40°C for 2 h. The bottle was removed from the bath and the slurry mixed using a Yamato mixer at low rpm or an attrition scrubber for 1 h at ambient temperature (approximately 25°C). The bottle was placed back into the water bath at 40°C for 2 h. The slurry was transferred to 1 L polyethylene bottles and centrifuged at 2500 rpm for 15 min. The supernatant was decanted and the solids repulped with 600 mL of potable water. The slurry was centrifuged at 2500 rpm for 15 min and the supernatant decanted. This rinsing (repulping) procedure was repeated for a total

of two rinse cycles.

Sulfuric Acid System

During the testing of the acid simulated soil washing system, extraction, 1200 mL of potable water was added to 600 g of soil in a 2.2 L Teflon bottle. The soil-extractant slurry was shaken for approximately 1 min, and placed into a constant-temperature water bath at 40°C for 2 h. The bottle was removed from the bath and the slurry mixed using a Yamato mixer at low rpm for 1 h at ambient temperature (approximately 25°C). During this stage of mixing, concentrated sulfuric acid was added to the slurry to achieve a pH of 1.5 to 2.0. The bottle was placed back into the water bath at 40°C for 2 h. The slurry was transferred to 1 L polyethylene bottles and centrifuged at 2500 rpm for 15 min. The supernatant was decanted and the solids repulped with 600 mL of potable water. The slurry was centrifuged at 2500 rpm for 15 min and the supernatant decanted. This rinsing (repulping) procedure was repeated for a total of two rinse cycles.

3.5.3 Equipment and Materials

The simulated soil washing system set up in the FERMCOT treatability laboratory, was designed to simulate operational parameters proposed in the PFD for a full-scale soil washing system. The simulation focused mostly on reaction time, soil:extract or soil:rinsing water ratios, extraction temperature, chemical extractant concentration, and rinse cycles. The equipment used in the laboratory testing consisted of 2.2 L Teflon reactor bottles, constant-temperature water bath, and an International Equipment Company (IEC) Model K centrifuge for solid-liquid phase separation.

3.5.4 Sampling and Analysis

All analyses were conducted by a contracted

laboratory for a full radiological, inorganic and organic analytes. Soil samples collected for initial characterization were aliquoted from the 5-gal buckets containing the homogenized soil from each location. Only one sample was analyzed for the AS-1 through AS-3 soil. The AS-4 through AS-9 soil were analyzed in duplicate. A single replication was analyzed for all extracted soil.

3.5.5 Data Management

All data from contracted laboratory analyses, received by FERMCO, was entered directly into the FACTS system following data validation. Validated data was electronically transferred from the FACTS to the Sitewide Environmental Database (SED). Total data reports and summary data reports, contained in the attachments, are generated directly from the SED.

4.0 RESULTS AND DISCUSSION

4.1 Initial Characterization

Table 4-1 lists the 12 soil, acronym identifier, initial total uranium concentration, and whether other COCs were present. Figure 4-1 shows the location of the 12 soil within the FEMP. Total uranium values were calculated from isotopic U-238 using a conversion constant for activity to concentration of 2.98. Total uranium concentrations for the ID-A, ID-B, and Operable Unit 5-A soil are for composite samples taken from the 55-gallon drums. Selected quantities of these three soil were taken from these prepared drummed soil and further homogenized and characterized before use in bench-scale testing. The ID-A, ID-B, and Operable Unit 5-A soil were used in bench-scale testing conducted at an IT laboratory. ID-A and ID-B soil were used in pilot-scale testing at the FEMP. The remaining nine soil (AS-1 through AS-9) were used solely for additional bench-scale testing in

support of an investigation of a wider range of FEMP soil with a wider range of COCs and total uranium concentrations. All twelve soil were used in additional bench-scale testing conducted at the FEMP during the final stages of treatability testing.

4.2 Bench-Scale Tests

4.2.1 Stage 1: Physical Separation Tests

4.2.1.1 *Initial Analysis and Characterization Soil*

Soil from two of the five sites investigated in the characterization report by Lee and Marsh (1992) were selected for use in bench-scale tests. These soil were initially considered to be representative of the soil/contaminant matrix found on the FEMP site. Geotechnical characteristics of the two soil are presented in Table 4-2. The most interesting aspect to

TABLE 4-1

LIST OF TWELVE SOILS SHOWING LOCATION WITHIN THE FEMP, ACRONYM IDENTIFIER, INITIAL TOTAL URANIUM CONCENTRATION, AND WHETHER OTHER COCs WERE PRESENT

Soil Acronym	Soil Location	Total Uranium (mg kg ⁻¹)	Other COCs Present?
ID-A ^a	Incinerator	499	NO
ID-B ^a	Plant 1 Storage Pad	536	NO
OU5-A ^a	Maintenance Building	199	YES
AS-1	Plant 9	190	NO
AS-2	Plant 2/3	254	NO
AS-3	Plant 6	1490	NO
AS-4	Pilot Plant	85	YES
AS-5	Graphite Furnace	98	NO
AS-6	Paddys Run	27	NO
AS-7	KC-2 Warehouse	52	YES
AS-8	D&D Facility	52	YES
AS-9	Building 77/79	54	NO

^a Initial total uranium values for drum soil; values will vary from initial values determined for individual amounts used in selected treatability testing.

UNITED STATES
NAVY
HAMILTON CO.

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INDICATES SOIL LOCATIONS

these soil, considering that physical separation treatment is being investigated as the primary mechanism for soil/contaminant separation and ultimately volume reduction, is the high silt (0.053 - 0.002 mm) and clay (less than 0.002 mm) content. Both soil are comprised of approximately 60 percent silt and 15 percent clay.

Initial average total uranium concentrations were determined by analyzing six aliquots each of the final homogenized whole soil. The ID-A and ID-B soil were determined to have 497.6 [standard deviation (SD) equals 60.3] and 450.8 (SD equals 36.6) mg kg⁻¹ total uranium, respectively. This compared favorably to the 538 and 446 mg kg⁻¹ total uranium values for the ID-A and ID-B whole soil analyzed in a parallel treatability study conducted by the ORNL (Francis et al., 1993).

Different methods for digestion and analysis

of uranium in soil can contain a certain amount of inherent variability. The ORNL noted three analytical methods for determining total uranium in FEMP soil samples. The three methods, neutron activation, wet digestion, and radiocounting, produced values of 538, 470, and 543 mg kg⁻¹, respectively, for the ID-A soil and 446, 387, and 421 mg kg⁻¹, respectively, for the ID-B soil (Francis, et al. 1993). Initial total uranium concentration values of 497 and 451 mg kg⁻¹ determined in this bench-scale work, using wet digestion with IC detection, compares favorably to the values for whole soil from the parallel treatability study conducted by ORNL.

The concentration and distribution of uranium within the various size fractions for the ID-A and ID-B soil are given in Table 4-3. Soil were shaken for 30 minutes in a 4:1 potable water to soil slurry. Low particle size load values for total uranium in the 19 to 9.5 mm

TABLE 4-2

GEOTECHNICAL PARAMETERS FOR ID-A AND ID-B SOIL RECEIVED BY THE LABORATORY FROM THE FEMP SITE

Soil Separates	Parameter	Analytical Methods	Soil Location	
			Incinerator Soil (ID-A)	Plant 1 Pad Soil (ID-B)
Gravel	>2 mm (%)	ASTM ^c D 422	4.6	2.1
Sand	2 mm - 0.05 mm (%)	ASTM D 422	18.0	23.3
Silt	0.05mm - 0.002 mm (%)	ASTM D 422	62.4	58.6
Clay	<0.002mm (%)	ASTM D 422	15.0	16.0
	Specific gravity	ASTM D 854	2.67	2.74
	Liquid Limit	ASTM D 4318	26.0	34.0
	Plasticity Index	ASTM D 4318	8.0	18.0
	CEC ^a (meq ^b /100 g)	SW-846 ^d (9081)	19.3	19.2
	Water Content (%)	ASTM D 2216	21.8	14.1

^aCEC - Cation Exchange Capacity

^bmeq - milliequivalents

^cASTM - American Society for Testing and Materials

^dEPA SW-846 - Test Methods for Evaluating Solid Waste

and 9.5 to 2 mm particle size fractions were noted for ID-A (3.2 and 6.3 mg kg⁻¹, respectively) and ID-B (0 and 2.1 mg kg⁻¹, respectively) soil. Since the percentage of total uranium contributed by these two size fractions for both soil was relatively insignificant, subsequent tests involving the effectiveness of various dispersants as extracting reagents were focused only on the less than 2mm soil size fractions. Particle size load values for total uranium among the sand, silt, and clay size fractions ranged from 64.9 to 195 mg kg⁻¹ for ID-A and 54.4 to 171 mg kg⁻¹ for ID-B.

4.2.1.2 Chemical Dispersant/Extractant Study

Four sodium reagents used as dispersants were compared to potable water on their effective-

ness in deflocculating aggregates and removing uranium from each of the resulting soil size fractions. The ID-A and ID-B soil used in the study had initially been dry screened through a 2-mm sieve. Table 4-4 shows the percentage of soil in each size fraction resulting from potable water and the 1mM dispersing solutions. Comparison of the particle distribution in this table with those values derived from the ASTM standard analytical method (see Table 4-2) indicates some discrepancy for individual textural classes, particularly the sand and clay fractions. Since the data in Table 4-2 is considered to be the baseline geotechnical data for the two whole soil, the low percentage of sand for the ID-A soil is considered an anomaly and probably results from of the initial drying and sieving

TABLE 4-3

**CONCENTRATION AND DISTRIBUTION OF TOTAL URANIUM IN
SELECTED PARTICLE SIZE FRACTIONS USING A SOIL WATER
SLURRY^a FOR ID-A AND ID-B HOMOGENIZED WHOLE SOILS
FROM THE FEMP SITE**

Soil Location	Particle Size Distribution (mm)	% Fraction in Size Distribution	Uranium Concentration (mg kg ⁻¹)	Particle Size Load (mg kg ⁻¹)	% Uranium Contribution by Size Fraction
ID-A Incinerator Area	Whole Soil	NA ^b	497	NA	NA
	19 - 9.5	20.1	16	3.2	0.8
	9.5 - 2	1.5	420	6.3	1.6
	2 - 0.053	12.5	1028	128	32.2
	0.053 - 0.002	61.5	317	195	49.1
	<0.002	4.4	1475	64.9	16.3
ID-B Plant 1 Pad Area	Whole Soil	NA	450	NA	NA
	19 - 9.5	0.0	0	0	0.0
	9.5 - 2	3.1	66	2.1	0.6
	2 - 0.053	28.8	189	54.4	14.9
	0.053 - 0.002	61.8	223	138	37.8
	<0.002	6.3	2710	171	46.7

^a4:1 potable water to soil slurry shaken for 30 minutes

^bNA - not applicable

procedures (Section 2.2). The low clay content for all solutions except CBD is considered to result from the inability for those solutions or the 30-minute shake procedure to provide complete dispersion of the aggregates.

The distribution of uranium among the size fractions for both soil indicate that simple physical separation, even with a dilute chemical dispersing solution, does not result in any size fraction that has an acceptably low concentration of uranium. The uranium concentration is highest in the sand and clay fractions for the ID-A soil and the clay fraction for the ID-B soil. One of the most important factors relative to uranium distribution in these two soil is that the silt fraction, which constitutes nearly two-thirds of the soil mass, contains uranium concentrations between 250 and 300 mg kg⁻¹, regardless of the dispersing solution. This is well above an acceptable uranium level

for treated soil.

Table 4-5 contrasts the effects of potable water and dispersing solutions (the values are averaged across the four dispersants tested) on the concentration and distribution of uranium in the three size fractions for the less than 2 mm ID-A and the ID-B soil. The use of dispersants increased the percent of the silt fraction while decreasing the percent sand fraction, indicating an enhanced effect on aggregate dispersion. The loading factor for uranium also seems to have shifted from the sand and silt fractions in both soil to the clay fraction as a result of the dispersing solutions. In the case of the ID-A soil, the uranium load value for the sand fraction decreased from 460 to 182 mg kg⁻¹ by using dispersing solutions. The uranium load values in the clay fraction of the ID-B soil increased from 79 to 192 mg kg⁻¹ with the addition of dispersing reagents.

TABLE 4-4

PARTICLE SIZE DISTRIBUTIONS AND URANIUM CONCENTRATIONS FOR THE LESS THAN 2-mm ID-A AND ID-B SOILS RESULTING FROM WATER AND FOUR 1mM DISPERSING REAGENT SOLUTIONS^a

Soil Location	Dispersing Reagent	Soil Size Fraction (mm)					
		2 - 0.053		0.053 - 0.002		<0.002	
		Soil Fraction (%)	Total Uranium (mg kg ⁻¹)	Soil Fraction (%)	Total Uranium (mg kg ⁻¹)	Soil Fraction (%)	Total Uranium (mg kg ⁻¹)
ID-A Incinerator Area	H ₂ O	23.3	1970	72.6	340	4.1	883
	NaOH	11.6	1566	83.0	265	5.4	1303
	Na ₂ CO ₃	9.4	1610	85.8	267	4.8	2017
	NaHCO ₃	9.3	2202	85.6	300	5.1	1295
	CBD	10.7	1713	78.3	227	11.0	913
ID-B Plant 1 Pad Area	H ₂ O	38.4	228	55.1	273	6.5	1219
	NaOH	27.6	231	66.4	270	6.0	2293
	Na ₂ CO ₃	28.3	214	67.3	247	4.4	3577
	NaHCO ₃	27.1	248	68.6	279	4.3	3244
	CBD	28.1	186	56.3	281	15.6	999

^a Solutions were 1:4 soil/dispersing solution ratios shaken for 30 minutes.

The effect of using a sodium reagent on the distribution of uranium among the three size fractions is shown in Table 4-5. The shift in uranium contribution by size fraction from sands to the clays indicates a redistribution of uranium or uranium-bearing particles (e.g., clay films). After using water, 61.9 percent of the uranium remained with the ID-A soil sand fraction while only 4.8 percent was associated with the ID-A soil clay fraction. However, with the use of dispersants, only 36.9 percent of the uranium was associated with the sand fraction while 18.5 percent was now associated with the clay fraction. This is also evident in the ID-B soil, where the amount of

uranium associated with the clay fraction increased from 25 percent to 45.1 percent.

4.2.1.3 Attrition Scrubbing Tests

The results of the dispersant/extractant tests provided distribution characteristics for uranium relative to individual particle size fractions; however, these tests did not identify any soil fraction for either the ID-A or ID-B soil that reduced uranium to acceptable residual levels. In an effort to simulate physical separation processes common to the soil washing technology, alkaline reagents were combined with mechanical mixing and tested

TABLE 4-5

**CONCENTRATION AND DISTRIBUTION OF URANIUM IN THE
THREE SIZE FRACTIONS OF THE LESS THAN 2mm ID-A AND
ID-B SOILS USING WATER AND DISPERSANTS**

Soil Location	Particle Size Distribution (mm)	% Fraction in Size Distribution	Uranium Concentration (mg kg ⁻¹)	Particle Size Load (mg kg ⁻¹)	Uranium Contribution by Size Fraction
<u>Water</u>					
ID-A	2 - 0.053	23.3	1970	460	61.9
Incinerator	0.053 - 0.002	72.6		237	33.3
Area	<0.002	4.1	340	35	4.8
			883		
ID-B	2 - 0.053	38.4	228	87	27.6
Plant 1	0.053 - 0.002	55.1	273	150	47.4
Pad	<0.002	6.5	1219	79	25.0
<u>Dispersing Solutions (Averaged)</u>					
ID-A	2 - 0.053	10.3	1773	182	36.9
Incinerator	0.053 - 0.002	83.1	264	220	44.6
Area	<0.002	6.6	1382	91	18.5
ID-B	2 - 0.053	27.8	219	61	14.3
Plant 1	0.053 - 0.002	64.6	269	173	40.6
Pad	<0.002	7.6	2528	193	45.1

for their effectiveness in removing uranium from the soil.

Attrition scrubbing tests were conducted on the less than 2 mm size fraction for ID-A and ID-B soil using water and three alkaline extraction solutions common to the uranium mining and processing industry: sodium carbonate/sodium bicarbonate, ammonium carbonate/ammonium bicarbonate, and sodium pyrophosphate. The test design was structured to target extractant, extraction solution concentration, and attrition scrubbing time effects on uranium and activity removal from two soil size fractions (less than 0.053 mm and greater than 0.053 mm).

ID-A Soil

Figures 4-2 through 4-4 illustrate the effect of alkaline extractants on removing uranium from two size fractions of the ID-A soil. Figure 4-2 shows the effect of the sodium pyrophosphate concentration and attrition scrubbing time on uranium concentration for the less than 0.053 mm and greater than 0.053 mm soil.

The most striking feature about Figure 4-2 is the large difference in uranium concentration between the two size fractions. The greater than 0.053 mm (sand) fraction contains roughly four to six times the concentration of uranium than the less than 0.053 mm (silt and clay) size fraction. However, only 18 percent of the ID-A soil falls within the sand fraction (Table 4-2).

Increasing the concentration of dispersant generally resulted in a decreasing concentration of uranium within all attrition scrubbing times. The effect was most pronounced for the greater than 0.053 mm soil fraction during the 5 minute attrition scrubbing test. The graph illustrates an overall similar effect within all attrition scrubbing times for both soil fractions. Holding the extractant concen-

FIGURE 4-2. THE EFFECT OF SODIUM PYROPHOSPHATE CONCENTRATION AND ATTRITION SCRUBBING TIME ON URANIUM CONCENTRATION OF TWO PARTICLE-SIZE FRACTIONS FOR ID-A SOIL.

tration constant, a similar pattern exists for attrition scrubbing time, where increasing the attrition scrubbing time increases the amount of uranium removed.

One can evaluate an optimum set of conditions for removing uranium while minimizing concentration and scrubbing time by proceeding from the far back corner of the graph (least aggressive conditions) diagonally forward towards the front corner of the graph (most aggressive conditions). Sands seem to reach optimum operation conditions at about 15 minute extraction time for the 0.25 M concentration. This means that little uranium is further removed by increasing scrubbing time to 30 minutes or extractant concentration to 0.5 M. Although less pronounced, the same scenario exist for the silt and clay fractions.

Figure 4-3 illustrates the effect of ammonium carbonate/bicarbonate concentration and attrition scrubbing time on uranium concentration of the two soil fractions for the ID-A

soil. Five minutes of scrubbing in a 33 percent solids slurry and water resulted in the sand fraction at approximately 1500 mg kg^{-1} uranium and the silt and clay fraction at 250 mg kg^{-1} . Increasing scrubbing time to 15 minutes and carbonate concentration to 0.25 M decreased uranium concentration in the sand fraction to 571 mg kg^{-1} . Increasing scrubbing time to 30 minutes and extractant concentration to 0.5 M only reduced uranium concentration from 571 to 526 mg kg^{-1} (8 percent). The effect of ammonium carbonate/bicarbonate on the less than 0.053 mm soil fraction was once again less pronounced. The best effect was achieved by simply increasing the extractant concentration to 0.25 M. This reduced uranium concentration in the silt and clay fractions from approximately 250 to 145 mg kg^{-1} , approximately 40 percent.

The pattern for uranium extraction from the sand fraction using sodium carbonate/bicarbonate (Figure 4-4) is not as defined as for the other extractants. Still, the 0.25 M concentra-

tion was one of the most effective; however, it required 30 minutes of attrition scrubbing. The results for the less than 0.053 mm soil fraction were similar in pattern to the previous two extractants. Nearly 60 percent of the uranium was removed by a 0.25 M solution during 15 minutes of scrubbing.

ID-B Soil

Figures 4-5 through 4-7 illustrate the effect of alkaline extractants on removing uranium from two size fractions of the ID-B soil. The ID-B soil, much like the ID-A soil, has a low amount of sand (23 percent) and a high amount of silt (58 percent) and clay (16 percent). Comparison of the data for the ID-B soil with the ID-A soil brings out one very prominent feature; the high levels of uranium are associated with the less than 0.053 mm soil fraction, rather than the greater than 0.053 mm soil. The uranium concentration in the silt and clay fraction is on an average approximately two to three times the uranium level on the sand fraction. Also, the levels of uranium

FIGURE 4-3. THE EFFECT OF AMMONIUM CARBONATE/BICARBONATE CONCENTRATION AND ATTRITION SCRUBBING TIME ON URANIUM CONCENTRATION OF TWO PARTICLE-SIZE FRACTIONS FOR ID-A SOIL.

FIGURE 4-4. THE EFFECT OF SODIUM CARBONATE/BICARBONATE CONCENTRATION AND ATTRITION SCRUBBING TIME ON URANIUM CONCENTRATION OF TWO PARTICLE-SIZE FRACTIONS FOR ID-A SOIL.

concentration within any size fraction does not exceed 500 mg kg⁻¹. These two features clearly illustrate the differences between the two soil relative to the effectiveness that physical separation and chemical extraction treatments might have.

Figure 4-5 shows the effect of sodium pyrophosphate concentration and attrition scrubbing time on uranium concentration for the less than 0.053 mm and greater than 0.053 mm size fraction for the ID-B soil. Attrition scrubbing time had no effect on either soil fraction with water. Increasing the concentration of dispersant generally resulted in a decreasing concentration of uranium within all attrition scrubbing times for both soil size fractions. The effect was most pronounced for the less than 0.053 mm soil fraction during the 5 minute attrition scrubbing test, where the uranium concentration was reduced from 330 to 65 mg kg⁻¹, a reduction of almost 80 percent. The graph illustrates an overall similar effect within all attrition scrubbing times for both soil fractions.

Once again, one can evaluate an optimum set of conditions for removing uranium while minimizing concentration and scrubbing time by proceeding from the far back corner of the graph (least aggressive conditions) diagonally forward towards the front corner of the graph (most aggressive conditions). Both soil fractions seem to reach optimum operation conditions at about 15 minutes extraction time for the 0.25 M concentration.

Figure 4-6 illustrates the effect of ammonium carbonate/bicarbonate concentration and attrition scrubbing time on uranium concentration of the two soil fractions for the ID-A soil. Little difference was noted for 5 minute attrition scrubbing, regardless of extractant concentration. However, when the scrubbing time was increased to 15 minutes, a 0.1 M solution was very effective, removing almost

FIGURE 4-5. THE EFFECT OF SODIUM PYROPHOSPHATE CONCENTRATION AND ATTRITION SCRUBBING TIME ON URANIUM CONCENTRATION OF TWO PARTICLE-SIZE FRACTIONS FOR ID-B SOIL.

78 percent of the uranium. The effect of ammonium carbonate/bicarbonate on the greater than 0.053 mm soil fraction was less pronounced, with an overall average reduction of only about 20 to 30 percent, regardless of attrition scrubbing time or extractant concentration. The pattern for uranium extraction from the silt and clay fractions using sodium carbonate/bicarbonate (Figure 4-7) is similar to the other extractants. Still, the 0.25 M concentration and 15 minute scrubbing time was one of the most effective for the both soil fractions.

4.2.2 Stage I: Chemical Extraction Tests

4.2.2.1 Initial Analyses and Characterization of Soil

An initial analysis and characterization of two soil considered to be representative of the soil/contaminant matrix found at the FEMP site was conducted before their use in bench-scale

FIGURE 4-8. URANIUM CONCENTRATION IN ID-A AND ID-B EXTRACTED SOILS FOR TWELVE EXTRACTANTS.

29.1 and 29.1 mg kg⁻¹, respectively. EDTA was more effective at the high pH range (pH 10 and pH 8), reducing uranium concentration to 24.3 and 34.6 mg kg⁻¹, respectively.

Figures 4-9 and 4-10 illustrate the percent of total uranium in extracted soil solids, spent extract, and rinsate for each of the extractants for ID-A and ID-B soil, respectively. The inorganic acids resulted in over 95 percent reduction in uranium concentration in the solid phase of both soil. EDTA (pH 10) was also able to achieve a greater than 90 percent reduction in uranium concentration in both soil. The carbonate compounds, sodium hydroxide and EDTA were the next most effective chemical extractants for ID-A soil, removing better than 70 percent of the total uranium. However, sodium carbonate, ammonium carbonate, sodium hydroxide, and EDTA (pH 8 and pH 10) were very effective in ID-B soil, reducing total uranium concentration in the solids to less than 50 mg kg⁻¹,

equating to more than a 90 percent reduction in total uranium. EDTA's effectiveness seemed to be pH dependent. Figures 4-9 and 4-10 illustrate that the rinsate accounts for less than 10 percent of the total uranium removed during the extraction process. However, an additional 10 percent would remove 50 and 45 mg kg⁻¹ from ID-A and ID-B soil, respectively.

4.2.2.3 Phase II: Screening of Selected Extractants

The inorganic acids were the most effective extractants of the reagents tested. Therefore, three inorganic acids (sulfuric, nitric, and hydrochloric) were selected from Phase I testing for further evaluation in Phase II testing on their effectiveness in removing total uranium from the two soil. Each extractant was tested at five concentrations to determine the lowest concentration of extractant that

FIGURE 4-9. THE PERCENT OF TOTAL URANIUM IN EXTRACTED SOIL SOLIDS, SPENT EXTRACTANT, AND RINSATE FOR ID-A SOILS FOLLOWING EXTRACTION, FOR TWELVE EXTRACTANTS.

FIGURE 4-10. THE PERCENT OF TOTAL URANIUM IN EXTRACTED SOIL SOLIDS, SPENT EXTRACTANT, AND RINSATE FOR ID-B SOILS FOLLOWING EXTRACTION, FOR TWELVE EXTRACTANTS.

could be used without significantly diminishing the amount of total uranium removed from the extracted solids. The extraction time (4 hours), temperature (80°C), and dose rate (10 percent solids) were kept the same as in Stage I testing. Figure 4-11 shows the effect of five concentrations of sulfuric acid on uranium concentration in ID-A and ID-B soil following chemical extraction. All sulfuric acid concentrations, except for 0.2 N, were able to achieve less than 50 mg kg⁻¹ total uranium in the extracted solids (greater than 90 percent reduction in total uranium).

The ineffectiveness of the 0.2 N solution may be a result of the buffer capacity of the ID-A soil and the resulting neutralization of the added acid. Increasing the concentration beyond 1 N did not reduce total residual uranium concentration in the soil beyond the 14 mg kg⁻¹. The ID-B soil was responsive to all concentrations of sulfuric acid. Increasing acid concentration from 1 N to 2 N reduced

total uranium concentration in the extracted solids from 18 to 8 mg kg⁻¹. Overall, sulfuric acid concentration in excess of 1.0 N resulted in little additional uranium being removed from either the ID-A or ID-B soil.

The concentration of total uranium in extracted ID-A and ID-B soil following chemical extraction for five concentrations of nitric acid is illustrated in Figure 4-12. Much like the results for sulfuric acid extraction, a 1.0 N nitric acid concentration was necessary to achieve less than 50 mg kg⁻¹ total uranium concentration in both soil. A 1 N acid strength reduced total uranium concentration in extracted solids to 9 mg kg⁻¹ for both soil. Increasing the concentration of nitric acid to 5.3 and 8.0 N resulted in less than 1 percent additional uranium removal from either soil.

Figure 4-13 shows the concentration of total uranium in extracted ID-A and ID-B soil

FIGURE 4-11. THE CONCENTRATION OF TOTAL URANIUM IN EXTRACTED ID-A AND ID-B SOILS FOLLOWING CHEMICAL EXTRACTION FOR FIVE CONCENTRATIONS OF SULFURIC ACID.

following chemical extraction for five concentrations of hydrochloric acid. A 1 N hydrochloric acid solution, much like sulfuric and nitric acids, was slightly more effective on ID-B soil than ID-A soil, reducing total uranium concentrations to 8 and 14 mg kg⁻¹, respectively. Additional acid strengths beyond 1.0 N resulted in little additional removal of total uranium from the extracted solids.

FIGURE 4-12. THE CONCENTRATION OF TOTAL URANIUM IN EXTRACTED ID-A AND ID-B SOILS FOLLOWING CHEMICAL EXTRACTION FOR FIVE CONCENTRATIONS OF NITRIC ACID.

The distribution of total uranium among the extracted soil, spent extractant, and rinse water for ID-A and ID-B soil following extraction, with five concentrations of sulfuric acid, nitric acid, and hydrochloric acid is shown in Figures 4-14 and 4-15. Figure 4-14 illustrates that at lower acid concentrations, over 90 percent of the uranium remained in the extracted solids for the ID-A soil. This ineffectiveness in total uranium extraction at lower concentrations is not evident in the ID-

FIGURE 4-13. THE CONCENTRATION OF TOTAL URANIUM IN EXTRACTED ID-A AND ID-B SOILS FOLLOWING CHEMICAL EXTRACTION FOR FIVE CONCENTRATIONS OF HYDROCHLORIC ACID.

B soil (Figure 4-15). The amount of uranium removed in the rinsate for all three acids and both soil never exceeded 10 percent of the total uranium. However, as noted previously, a 10 percent reduction in the amount of additional uranium can potentially remove as much as 50 mg kg⁻¹.

4.2.2.4 Phase III: Time, Temperature, and Concentration Study

Two of the inorganic acids tested in Phase II were carried over to Phase III testing. The effects of sulfuric and nitric acids at two dose rates, two extraction times, and two temperatures are illustrated in Figure 4-16 for the ID-A soil. The optimum interactive effects of time, temperature, and dose rate for each acid can be evaluated from this figure. The least aggressive condition (e.g., 4:1 dose rate, 0.5 hour extraction time, ambient temperature, and 1 N concentration) are near the back corner of the graph. By proceeding from the

FIGURE 4-14. THE PERCENT URANIUM CONCENTRATION IN EXTRACTED SOIL, SPENT EXTRACTANT, AND RINSE WATER FOR ID-A SOIL FOLLOWING EXTRACTION WITH FIVE CONCENTRATIONS OF SULFURIC, NITRIC, AND HYDROCHLORIC ACIDS.

FIGURE 4-15. THE PERCENT URANIUM CONCENTRATION IN EXTRACTED SOIL, SPENT EXTRACTANT, AND RINSE WATER FOR ID-B SOIL FOLLOWING EXTRACTION WITH FIVE CONCENTRATIONS OF SULFURIC, NITRIC, AND HYDROCHLORIC ACIDS.

far back corner of the graph diagonally forward towards the front corner, the extraction conditions become more aggressive. Figure 4-16 shows that nitric acid had a pronounced effect on total uranium removal when the extraction temperature was increased from ambient to 40°C. On the average, an additional 50 mg kg⁻¹ of total uranium was removed from the ID-A soil by increasing the temperature. Although increasing the acid concentration from 1 N to 2 N at ambient temperature did not influence uranium extraction, it did seem to enhance total uranium extraction at 40°C. Increasing the reaction time from 0.5 to 2 hours and/or increasing the dose rate from 4:1 (20 percent solids) to 7:1 (12.5 solids) did not show a similar effect on reducing the total uranium concentration in the extracted solids. A 1 N nitric acid solution at 40°C and a 7:1 dose rate and 0.5 hour extraction time was able to reduce total uranium concentration in the ID-A extracted soil to 26 mg kg⁻¹.

FIGURE 4-16. THE EFFECT OF NITRIC ACID AND SULFURIC ACID CONCENTRATIONS, TEMPERATURE, EXTRACTION TIME AND DOSE RATE ON URANIUM CONCENTRATION IN EXTRACTED ID-A SOIL.

Increasing the temperature from ambient to 40°C during sulfuric acid extraction reduced the total uranium concentration in the extracted solids an additional 30 mg kg⁻¹ (Figure 4-16). Increasing acid strength from 1 N to 2 N for either temperature did not seem to have much effect on the final concentration of total uranium in extracted soil solids. Overall, dose rate and extraction time did not seem to influence total uranium extraction for sulfuric acid in ID-A soil. Based on this data, 1 N and 2 N sulfuric acid solutions at 40°C and a 4:1 dose rate and 0.5 hour reaction time were able to reduce total uranium concentration in the extracted soil to 38 and 36 mg kg⁻¹, respectively.

Figure 4-17 illustrates the effect of nitric acid and sulfuric acid concentrations, temperature, extraction time, and dose rate on total uranium concentration in extracted ID-B soil. It is obvious that 1 N nitric acid solutions at a 4:1 dose rate, regardless of temperature or extraction time, did not affect total uranium concentration in extracted solids. A 2 N nitric acid solution at 40°C was extremely effective, regardless of dose rate or extraction time. The most aggressive and effective extraction conditions were a 2 N nitric acid solution at 40°C, 7:1 dose rate, and 2 hour extraction time. This treatment lowered the concentration of total uranium in the extracted soil to 17 mg kg⁻¹. However, decreasing acid concentration to 1 N and extraction time to 0.5 hour still resulted in a final concentration of total uranium in the extracted soil of 41 mg kg⁻¹.

Sulfuric acid was very effective on ID-B soil, regardless of extraction conditions. Only the least aggressive conditions for the 1 N and 2N sulfuric acid solutions (e.g., ambient, 4:1 dose rate, and 0.5 hour extraction time) resulted in a total uranium concentration in the extracted soil in excess of 50 mg kg⁻¹. The most aggressive conditions reduced total uranium concentration in the extracted soil solids to

FIGURE 4-17. THE EFFECT OF NITRIC ACID AND SULFURIC ACID CONCENTRATIONS, TEMPERATURE, EXTRACTION TIME AND DOSE RATE ON URANIUM CONCENTRATION IN EXTRACTED ID-B SOIL.

17 mg kg⁻¹. By reducing acid strength to 1 N and extraction time to 0.5 hour and maintaining 40°C temperature and a 7:1 dose rate, total uranium concentration in the extracted solids was only 19 mg kg⁻¹.

4.2.3 Stage II: Physical Separation and Chemical Extraction Tests

Based on the findings from initial physical separation and chemical extracting bench-scale testing, a final set of bench-scale tests were conducted to evaluate the selected soil washing treatment process before initiating pilot-scale testing. These tests were designed to evaluate a sequential treatment process that incorporated attrition scrubbing with sodium carbonate/sodium bicarbonate solution followed by a dilute sulfuric acid extraction.

All earlier bench-scale physical separation testing was conducted using a modified Hamilton Beach mixer. The experimental

design incorporated the use of a DECO attrition mill in the combined physical separation and chemical extraction test since the mill was considered to provide results comparable to the attrition scrubber designed into the soil washing pilot plant. Figure 4-18 illustrates the results from a comparative study conducted with a DECO attrition mill and a Hamilton Beach mixer. Although no replications were conducted to allow for a statistical analysis, visual comparison of the results indicate that uranium concentration for the two soil size fractions in treated ID-A and ID-B soil as a function of attrition scrubbing time are similar between the two pseudo-attrition scrubbers.

The DECO attrition mill was used in the combined process test to evaluate the effectiveness of a sequential physical separation and chemical extraction treatment process on removing uranium from the two soil. A 0.1 M sodium carbonate/sodium bicarbonate solution, 15 min attrition scrubbing time and 33

percent solids, reduced uranium concentration in the ID-A soil from 497 to 341 mg kg⁻¹ and in the ID-B soil and from 450 to 241 mg kg⁻¹. This equates to a 31 and 46 percent reduction in total uranium concentration.

These carbonate-attrition-scrubbed soil were centrifuged to separate the soil solids which were subsequently treated with a 2 N sulfuric acid solution at 40°C for 30 min. When a 4:1 dose rate (20 percent solids) was used, uranium concentrated in the treated solids was reduced to 52 and 92 mg kg⁻¹ for ID-A and ID-B soil, respectively. This equated to a 90 and 80 percent reduction in the initial uranium concentration for the ID-A and ID-B soil respectively. When a 7:1 dose rate (12.5 percent solids) was used, uranium concentration in the treated solids was reduced to 49 and 71 mg kg⁻¹ for ID-A and ID-B soil, respectively. This equated to a 90 and 85 percent reduction in the initial uranium concentration for the ID-A and ID-B soil respectively.

4.3 Pilot-Scale Tests

4.3.1 Operable Unit 5 Soil Washing Demonstration Tests

The soil washing pilot plant, located in Plant 8, was operated in a batch mode during the summer of 1993 for a period of three months. Figure 4-19 illustrates a simplified version of the soil washing process, previously given in detail in the PFDs provided in Section 3.4. This figure shows the primary process streams generated during the operation of the soil washing system. Potentially, six basic process streams could have been generated from operation of the pilot plant. Those streams included: (1) treated soil solids greater than 4.75 mm; (2) treated soil solids 0.3 to 4.75 mm; (3) treated soil solids 0.02 to 0.3 mm; (4) treated soil solids less than 0.02 mm; (5) a filter cake (residue); and (6) spent carbonate

FIGURE 4-18. A COMPARISON OF RESIDUAL CONCENTRATION OF URANIUM IN TWO SIZE FRACTIONS OF ID-A AND ID-B SOILS FOLLOWING ATTRITION SCRUBBING WITH A DECO ATTRITION MILL AND A HAMILTON BEACH MIXER.

As noted in Section 3.4.1.5, analytical support was provided by both the FERMCO laboratory and the contracted laboratory. The soil and uranium mass balancing for pilot plant operations was derived solely from FERMCO analytical data. Analyses performed by the contracted laboratory for the primary process streams included all radiological and inor-

Total uranium (the target analyte) concentration was determined by off-site analysis to be 499 and 536 mg kg⁻¹ for ID-A and ID-B, respectively. This was a composite analysis for all the fifteen 55-gallon drums of each soil prepared by the ID program. Specific total uranium analysis of each 55-gallon drum processed through the soil washing system was determined by on-site analysis to be 431 and 487 mg kg⁻¹ for the two drums of ID-A soil and 389 and 455 mg kg⁻¹ for the two drums of ID-B soil.

4.3.1.1 Physical Separation

The physical separation side of the soil washing pilot plant was designed with three principle components (trommel, screen deck, and centrifuge) to provide selected soil size fractions during processing operations. The trommel provided the first process stream by separating gravel greater than 4.75 mm from the soil. Only 3.7 (SD=0.6) and 0.7 (SD=0.3) percent of the initial soil mass fell into this size fraction for ID-A and ID-B, respectively. Although not analyzed for total uranium, this process stream was considered to be relatively low in total uranium concentration.

The centrifuge and screen deck were used to provide a feed to the attrition scrubber. The centrifuge provided a soil particle size fraction of approximately 0.02 mm. The screen deck was used as a protective step within the operation to remove a coarser fraction of the soil (greater than 0.3 mm) before centrifugation. The 0.3 to 4.75 mm soil solids from the screen deck averaged greater than 75 percent solids for both ID-A and ID-B soil. The centrifuge produced both a high solids stream and a high water stream (centrate). While the centrate was averaging approximately one percent solids, the 0.02 to 0.3 mm soil solids from the centrifuge averaged greater than 70 percent solids for both soil. These 0.02 to 0.3 mm soil solids from the centrifuge were combined with the 0.3 to 4.75 mm soil solids from the screen deck and processed through the attrition scrubber. This 0.02 to 4.75 mm soil solids was considered the second primary process stream. The centrate from the centrifuge, which also contained a significant amount of the soil mass (considered to primarily consist of the fine less than 0.02 mm soil fraction of the soil), was transferred directly to the chemical extraction vessel and represented the third primary process stream.

The centrifuge was designed to provide a coarse soil size fraction with significant mass to warrant the use of an attrition scrubber. In general, attrition scrubbing is recommended for particles greater than 0.075 mm (sand particles). However, grain size distribution for these two soil showed that only approximately 18 and 22 percent, respectively, of the ID-A and ID-B soil particles were greater than 0.075 mm. By directing the soil fraction greater than 0.02 mm to the attrition scrubber, approximately 40 to 45 percent of the total soil mass could be processed through attrition scrubbing. The attrition scrubbing of the finer sand fraction (0.05 to 0.075 mm) and the coarser silt fraction (0.02 to 0.05 mm) in conjunction with the 0.075 mm to 4.75 mm soil fraction was considered potentially effective since individual particles in these size fractions exhibited similar physical characteristics (e.g., the lack of elasticity, plasticity, and cohesive qualities).

Grain size distribution was determined for all batch runs of the centrifuge solids (as compared to the centrate) coming off of the centrifuge for each of the three cycles through the centrifuge. All the soil solids coming off the centrifuge were less than 75 μ m. However, approximately 70 percent and more of this soil mass was less than 0.02 mm. In most cases, over 10 percent of the soil solids coming off the centrifuge was in the clay size fraction (less than 0.002 mm). Although the centrifuge functioned well as a dewatering device, it did not provide the specific particle size fraction of 0.02 mm. Therefore, the soil processed through the attrition scrubber was probably more representative of the whole soil. All reference to this primary process stream will continue to be referred to as the greater than 0.02 mm soil fraction. All reference to the soil separates contained in the centrate will be referred to as the less than 0.02 mm soil fraction.

4.3.1.2 Soil Washing of the ID-A Soil

Tables 4-6 and 4-7 show the results and mass balances for soil and total uranium for individual soil washing process streams for the first and second drums respectively of the incinerator area soil. Each drum was processed separately and represented a single replication of the process operation. The two replications for each soil were used to evaluate reproducibility of process operations. The following is a discussion of the effectiveness of the soil washing process on the ID-A soil using average values and standard deviations (SD) calculated from data contained in Tables 4-6 and 4-7.

The total uranium concentrations in the greater than 0.02 mm and less than 0.02 mm treated soil solids were 27 mg kg⁻¹ (SD=1.4) and 62.5 mg kg⁻¹ (SD=26.2), respectively. These two primary process streams and the greater than 4.75 mm gravel accounted for an

average of 74.3 percent (SD=4.4) of the initial total mass for the ID-A treated soil solids.

This total mass of treated soil averaged 27 mg kg⁻¹ (SD=1.4). Residual total uranium mass remaining in the treated soil was approximately 10.3 percent (SD=0.4) of the total uranium mass contained in the feed soil. This equates to nearly a 90 percent reduction in total uranium mass for nearly 75 percent of the processed ID-A soil.

Most of the uranium mass which was either concentrated in the filter cake or remained in the spent carbonate extractant. The filter cake, which was the precipitate product from the spent sulfuric acid extractant, had a final total uranium concentration of approximately 637 mg kg⁻¹ (SD=209) and contained 11.2 percent (SD=3.5) of the total uranium mass. The final total uranium concentration in the treated spent sulfuric acid solution was approximately 5 µg L⁻¹. Most of the uranium remained in the spent carbonate solution.

TABLE 4-6

SOIL WASHING PILOT PLANT PROCESS STREAMS FOR INCINERATOR AREA SOIL (ID-A, RUN 1), SINGLE BATCH (DRUM) PROCESS

Process Streams	Total Mass (kg)	Total Mass (%)	Uranium (mg kg ⁻¹)	Uranium (mg)	Uranium (%)
Feed Soil	178.00	100.00	431	76,728	100.0
Treated Solids (> 4.75 mm)	5.78	3.25	NA ^a	NA	NA
Treated Solids (0.02 - 4.75 mm)	99.13	55.69	26	2,577	3.4
Treated Solids (< 0.02 mm)	32.95	18.51	44	1,453	1.9
Totals	137.86	77.45	29	4,030	5.3
Centrifuge Heel (avg.)	10.82	6.08	235	2,544	3.3
Filter Cake	13.02	7.31	489	6,367	8.7
Spent Carbonate Solution	44.03	NA	NA	63,546	82.8

^a NA - not applicable

TABLE 4-7**SOIL WASHING PILOT PLANT PROCESS STREAMS FOR INCINERATOR AREA SOIL (ID-A, RUN 2), SINGLE BATCH (DRUM) PROCESS**

Process Streams	Total Mass (kg)	Total Mass (%)	Uranium (mg kg ⁻¹)	Uranium (mg)	Uranium (%)
Feed Soil	181.28	100.00	487	88,222	100.0
Treated Solids (> 4.75 mm)	7.50	4.14	NA ^a	NA	NA
Treated Solids (0.02 - 4.75 mm)	102.04	56.29	28	2,857	3.2
Treated Solids (< 0.02 mm)	19.48	10.75	81	1,578	1.8
Totals	129.02	71.17	34	4,435	5.0
Centrifuge Heel (avg.)	13.57	7.49	219	2,969	3.3
Filter Cake	15.42	8.51	785	12,104	13.7
Spent Carbonate Solution	39.52	NA	NA	53,102	60.2

^aNA - not applicable

This solution contained 71.5 percent (SD=16) of the total uranium mass. This solution also contained a significant amount of the initial soil mass, although an exact value could not be calculated. Much of this soil mass contained the fine fraction of the soil separates that did not partition into the solid phase during centrifugation.

Figures 4-20 and 4-21 show the average reduction in total uranium concentration in the 0.02 to 4.75 and less than 0.02 mm soil solids, respectively, during Runs one and two of the ID-A soil treatment processes. Attrition scrubbing with carbonates reduced total uranium concentration in the 0.02 to 4.75 mm soil solids from 475 mg kg⁻¹ to less than 110 mg kg⁻¹. Total uranium concentration in this fraction was further reduced to 27 mg kg⁻¹ following 1 N sulfuric acid extraction. This sequential process resulted in a 95 percent reduction in total uranium for this size fraction of soil solids.

FIGURE 4-20. THE SEQUENTIAL REDUCTION IN TOTAL URANIUM CONCENTRATION IN THE 0.02 TO 4.75 mm ID-A SOIL SOLIDS DURING TREATMENT PROCESSES.

FIGURE 4-21. THE SEQUENTIAL REDUCTION IN TOTAL URANIUM CONCENTRATION IN THE < 0.02 ID-A SOIL SOLIDS DURING TREATMENT PROCESSES.

The centrate from the initial centrifuging of the undersize soil slurry from the screen deck was transferred directly to the reaction vessel

for chemical extraction. The average total uranium concentration in these less than 0.02 mm soil solids was 1186 mg kg⁻¹. Following a 1 N sulfuric acid extraction, the total uranium in this soil fraction was reduced to 995 mg kg⁻¹, equating to a 92 percent reduction in uranium concentration (Figure 4-21).

4.3.1.3 Soil Washing of the ID-B Soil

Tables 4-8 and 4-9 show the results and mass balances for soil and total uranium for individual soil washing process streams for the first and second drums respectively of the plant one pad area soil. Each drum of ID-B soil was processed separately and represented a single replication of the process operation. The two replications for each soil were once again used to evaluate reproducibility of process operations. The following is a discussion of the effectiveness of the soil washing process on the ID-B soil using average values and standard deviations calculated from data contained in Tables 4-8 and 4-9.

TABLE 4-8

SOIL WASHING PILOT PLANT PROCESS STREAMS FOR PLANT 1 PAD AREA SOIL (ID-B, RUN 1), SINGLE BATCH (DRUM) PROCESS

Process Streams	Total Mass (kg)	Total Mass (%)	Uranium (mg kg ⁻¹)	Uranium (mg)	Uranium (%)
Feed Soil	169.53	100.00	389	65,958	100.0
Treated Solids (> 4.74 mm)	1.14	0.67	0	0	0.0
Treated Solids (0.02-4.75mm)	61.43	36.24	14	860	1.3
Treated Solids (< 0.02 mm)	16.36	9.65	37	605	0.9
Centrifuge Heel (avg.)	40.59	23.94	46	1,849	2.8
Totals	119.52	70.50	28	3,314	5.0
Filter Cake	10.35	6.10	2,549	26,381	40.0

* NA - not applicable

TABLE 4-9**SOIL WASHING PILOT PLANT PROCESS STREAMS FOR PLANT 1 PAD AREA SOIL (ID-B, RUN 2), SINGLE BATCH (DRUM) PROCESS**

Process Streams	Total Mass (kg)	Total Mass (%)	Uranium (mg kg ⁻¹)	Uranium (mg)	Uranium (%)
Feed Soil	99.73	100.00	455	45,377	100.0
Treated Solids (> 4.74mm)	1.60	1.60	0	0	0.0
Treated Solids (0.02-4.75mm)	30.05	30.13	20	601	1.3
Treated Solids (< 0.02mm)	16.38	16.42	34	557	1.2
Centrifuge Heel (avg.)	37.36	37.46	73	2,729	6.0
Totals	85.39	85.62	46	3,887	8.5
Filter Cake	5.73	5.75	4,361	24,990	55.1
Spent Carbonate Solution	10.32	NA ^a	NA	6,916	15.2

^a NA - not applicable

The total uranium concentrations in the greater than 0.02 mm and less than 0.02 mm treated soil solids were 17 mg kg⁻¹ (SD=4.2) and 35.5 mg kg⁻¹ (SD=2.1), respectively. The centrifuge had provided an addition quantity of effectively treated soil constituting nearly 31 percent of the initial soil mass with a final total uranium concentration of 60 mg kg⁻¹ (SD=19.1). These three primary process streams and the greater than 4.75 mm gravel accounted for an average of 78 percent (SD=10.7) of the initial total mass for the ID-B treated soil solids. This total mass of treated soil averaged 37 mg kg⁻¹ (SD=12.7). Residual total uranium mass remaining in the treated soil was approximately 6.7 percent (SD=2.5) of the total uranium mass contained in the feed soil. This equates to over a 90 percent reduction in total uranium mass for nearly 78 percent of the processed ID-B soil.

Most of the uranium mass was either concentrated in the filter cake or remained in the spent carbonate extractant. The filter cake, which was the precipitate product from the

spent sulfuric acid extractant, had a final total uranium concentration of approximately 3455 mg kg⁻¹ (SD=1281) and contained 47.5 percent (SD=10.7) of the total uranium mass. The final total uranium concentration in the treated spent sulfuric acid solution was approximately 5 mg L⁻¹. A major portion of the uranium remained in the spent carbonate solution. This solution contained 23.5 percent (SD=11.8) of the total uranium mass. This solution also contained a significant amount of the initial soil mass, although an exact value could not be calculated. Much of this soil mass contained the fine fraction of the soil separates that did not partition into the solid phase during centrifugation.

Figures 4-22 and 4-23 show the sequential reduction in total uranium concentration in the 0.02 to 4.75 and less than 0.02 mm soil solids, respectively, during these treatment processes. These values are an average for Runs one and two of the ID-B soil. Attrition scrubbing with carbonates reduced total uranium concentration in the 0.02 to 4.75 mm soil solids from

FIGURE 4-22. THE SEQUENTIAL REDUCTION IN TOTAL URANIUM CONCENTRATION IN THE 0.02 TO 4.75 mm ID-B SOIL SOLIDS DURING TREATMENT PROCESSES.

FIGURE 4-23. THE SEQUENTIAL REDUCTION IN TOTAL URANIUM CONCENTRATION IN THE < 0.02 mm ID-B SOIL SOLIDS DURING TREATMENT PROCESSES.

198 mg kg⁻¹ to less than 41 mg kg⁻¹. Total uranium concentration in this fraction was further reduced to 28 mg kg⁻¹ following 1 N sulfuric acid extraction (Figure 4-22). This sequential process resulted in a 85 percent reduction in total uranium for this size fraction of soil solids.

The centrate from the initial centrifuging of the undersize soil slurry from the screen deck was transferred directly to the reaction vessel for chemical extraction. The average total uranium concentration in these less than 0.02 mm soil solids was 237 mg kg⁻¹. Following a 1 N sulfuric acid extraction, the total uranium in this soil fraction was reduced to 35 mg kg⁻¹, equating to an 85 percent reduction in uranium concentration (Figure 4-23).

4.3.1.4 TCLP and Comparative HSL Analyses for Primary Process Streams

Table 4-10 shows the total uranium values for ID-A and ID-B soil processed through the soil washing pilot plant for samples analyzed by the contracted laboratory and the FERMCO laboratory. The on-site analysis provided by the FERMCO laboratory supported the mass balancing of the process runs. The off-site analysis provided by the contracted laboratory supported TCLP analysis and tracking of other COCs. Table 4-10 compares total uranium analyses by the two laboratories and provides the TCLP analysis by the off-site laboratory for the primary process streams.

Total uranium concentration values for the initial soil and the primary process streams were consistently higher by off-site analysis as compared to on-site analysis. Table 4-10 shows that the average total uranium concentrations for the 0.02 to 4.75 mm process stream are 59 mg kg⁻¹ (SD=42) and 75 mg kg⁻² (SD=1.4) by the contracted laboratory, respectively, for the ID-A and ID-B soil. The average total uranium concentrations for the

TABLE 4-10**URANIUM VALUES BY TWO LABORATORIES FOR BOTH THE ID-A AND ID-B SOILS
PROCESSED THROUGH THE SOIL WASHING PILOT PLANT**

	Init Soil		> 4.75 mm		0.02 - 4.75 mm		< 0.02 mm		Filter Cake	
	HSL mg kg ⁻¹	TCLP µg L ⁻¹	HSL mg kg ⁻¹	TCLP µg L ⁻¹	HSL mg kg ⁻¹	TCLP µg L ⁻¹	HSL mg kg ⁻¹	TCLP µg L ⁻¹	HSL mg kg ⁻¹	TCLP µg L ⁻¹
ID-A Run 1 Contracted Lab	499 ^a	1206 ^a	NA	441	56	134	175	124	2083	855
FERMCO	431	NA	NA	NA	26	NA	44	NA	489	NA
ID-A Run 2 Contracted Lab	499 ^a	1206 ^a	NA	441	62	62	142	631	3516	3218
FERMCO	487	NA	NA	NA	28	NA	81	NA	785	NA
ID-B Run 1 Contracted Lab	536 ^b	11398 ^b	NA	NA	76	275	111	557	4350	117
FERMCO	389	NA	NA	NA	14	NA	37	NA	2549	NA
ID-B Run 1 Contracted Lab	536 ^b	11398 ^b	NA	NA	74	259	114	867	4738	21187
FERMCO	455	NA	NA	NA	20	NA	34	NA	4361	NA

^a One initial value was determined during initial characterization for ID-A soil^b One initial value was determined during initial characterization for ID-B soil

less than 0.02 mm process stream are 158 mg kg⁻¹ (SD=23.3) and 112 mg kg⁻¹ (SD=2.1) by the contracted laboratory, respectively, for the ID-A and ID-B soil, and 62 mg kg⁻¹ (SD=26.1) and 35 mg kg⁻¹ (SD=2.1) by the FERMCO laboratory, respectively, for the ID-A and ID-B soil.

The TCLP results indicate that there is a reduction in the leachable quantity of uranium for the 0.02 to 4.75 mm and the less than 0.02 mm process streams, as compared to the initial soil. The initial feed soil showed TCLP values of 3.6 and 33.9 mg L⁻¹ for the ID-A and ID-B soil, respectively. The 0.02 to 4.75 mm process stream was reduced to average TCLP values of 0.3 mg L⁻¹ (SD=0.15) and 0.8 mg L⁻¹ (SD=0.03) for the ID-A and ID-B soil, respectively. The less than 0.02 mm process stream was reduced to average TCLP values of 1.1 mg L⁻¹ (SD=1.1) and 2.1 mg L⁻¹ (SD=0.65) for the ID-A and ID-B soil, respectively.

4.4 COC Tests

The bench-scale soil washing test for COCs incorporated a test procedure that was modeled after the preliminary CRU5 CDR flow diagram for the proposed soil washing system. The six soil initially characterized and processed through a sulfuric acid process and a sodium carbonate/sodium bicarbonate process were ID-A, ID-B, OU5-A, AS-3, AS-4, and AS-7. The uranium concentrations for the soil before treatment and following an acid and a carbonate extraction process is given in Table 4-11.

All soil, except for soil the pilot plant area, resulted in residual uranium concentrations less than 113 mg kg⁻¹ following treatment with either sulfuric acid or sodium carbonate/sodium bicarbonate. All but one soil had initial TCLP values greater than 1.2 mg L⁻¹. The TCLP values for treated soil ranged from 8.6 mg L⁻¹ for carbonate-extracted Plant 6 soil (AS-3) to 0.15 mg L⁻¹ for KC-2 Warehouse soil (AS-7). However, there seems to be no

TABLE 4-11

URANIUM CONCENTRATIONS IN THE SOIL SOLIDS AND THE TCLP EXTRACT FOR SIX FEMP SOIL BEFORE TREATMENT AND FOLLOWING AN ACID AND A CARBONATE EXTRACTION PROCESS

Soil Locations	Initial Soil		Sulfuric Acid Process		Carbonate Extraction Process	
	HSL mg kg ⁻¹	TCLP µg L ⁻¹	HSL mg kg ⁻¹	TCLP µg L ⁻¹	HSL mg kg ⁻¹	TCLP µg L ⁻¹
ID-A	499	1.2	113	1.6	86	0.38
ID-B	536	11.4	28	0.51	44	2.2
OU5-A	199	2.1	113	5.6	113	0.68
AS-3	1490	---	277	---	357	8.6
AS-4	85	4.1	---	---	50	1.1
AS-7	52	0.38	23	0.15	51	0.44

relationship between TCLP values for treated soil and uranium concentration in soil solids before or following treatment.

The effectiveness of each chemical extraction process for soil with high uranium concentration (AS-3) and a soil with low uranium concentration (AS-7) is shown in Table 4-11. Sulfuric acid extraction reduced uranium in the AS-3 treated soil solids to 277 mg kg⁻¹ (81 percent reduction), while carbonate extraction reduced uranium concentration to 357 mg kg⁻¹ (76 percent reduction). The KC-2 Warehouse area soil, having an initial uranium concentration of 52 mg kg⁻¹, was treated to test the effectiveness of extractant process on soil with low uranium concentrations. Although carbonate extraction had no effect on removing uranium from this soil, sulfuric acid extraction removed 56 percent of the uranium to a final concentration of 23 mg kg⁻¹ in the treated solids.

Only two soils contained significant levels of other COCs, the Maintenance Building area soil (OU5-A) and the Pilot Plant area soil (AS-4). Only certain constituents are of potential concern in the groundwater pathway via vertical migration. The Maintenance Building area soil had elevated levels of certain inorganics (e.g., beryllium, chromium, and lead). The Pilot Plant area soils had elevated levels of chromium and lead. Lead concentration in both soils was unaffected by either a sulfuric acid or carbonate extraction process. Chromium levels were reduced in the AS-4 soil treated with sulfuric acid but were unaffected in the OU5-A soil.

REFERENCES

- American Society for Testing and Materials, 1991, "Standard Test Method for Particle-Size Analysis of Soils," Annual Book of ASTM Standards, Vol 04.08, American Society for Testing and Materials, Philadelphia, PA.
- dePercin, P., E. Bates, and D. Smith, 1991, "Designing Treatability Studies for CERCLA Sites: Three Critical Issues," J. of the Air and Waste Management Assn., Vol. 41, No. 45.
- Engineering News Record (ENR), "Tough Recipe at Toxic Cleanup Site," January 10, 1994.
- Francis, C.W., A.J. Mattus, M.P. Elless, and M.E. Timpson, 1993, Selective Leaching of Uranium From Uranium Contaminated Soils Using Carbonate- and Citrate-Based Leaching Solutions," Oak Ridge National Laboratory, ORNL/TM-12177, Oak Ridge, TN.
- Jackson, M.L., 1975, Soil Chemical Analysis - Advanced Course, 2nd ed., published by the author, Univ. of Wisconsin, Madison, WI.
- Kneff, D. W., G. Subbaraman, and R. J. Tuttle, 1992, "Homogeneity Evaluation of Fernald Soils Prepared For Treatability Studies," ETEC/GEN-ZR-0018. Energy Technology Engineering Center, Rocketdyne Division, Rockwell International, Los Angeles, CA.
- Kunze, M.E. and J.R. Gee, 1989, "Bench- and Pilot-Scale Case Studies for Metals and Organics Removals from CERCLA Site Soils," in Superfund '89, Proceedings of the 10th National Conference, Hazardous Materials Control Research Institute, pp. 207-215.
- Lahoda, E.J. and C.Y. Lin, 1993, "Fernald Soil Characterization and Treatability Study," Westinghouse Science and Technology Center (WSTC), Pittsburgh, PA.
- Lee, S.Y. and J.D. Marsh, Jr., 1992, "Characterization of Uranium-Contaminated Soils from DOE Fernald Environmental Management Project Site: Results of Phase I Characterization," Oak Ridge National Laboratory, ORNL/TM-11980, Oak Ridge, TN.
- Lee, S.Y., M.P. Elless, and F. Hoffman, 1993, "Solubility Measurement of Uranium in Uranium-Contaminated Soils," Oak Ridge National Laboratory, ORNL/TM-12401, Oak Ridge, TN.
- Mann, M. J. "Innovations in Soil Flushing/ Soil Washing Technologies: Task Group Findings" WASTECH '92 Symposium: Innovative Waste Remediation Technology "The State of the Art," October 30, 1992, San Diego, CA.
- "Minimum Additive Waste Stabilization Program: Soil Washing Report," 1993, Technology Applications Division, Lockheed Environmental Systems & Technologies Company (LEST), Las Vegas, NV.
- "Operational Procedure Report for the Fernald Soil Washing Pilot Plant Demonstration: Phase I, 1994, Treatability Group, Fernald Environmental Restoration Management Company (FERMCO), Cincinnati, OH.
- "Removal of Uranium from Uranium-Contaminated Soils, Phase I: Bench-Scale Testing," 1993, Uranium in Soils Integrated Demonstration Program, Soil Decon Task Group, Oak Ridge National Laboratory, ORNL-6762, Oak Ridge, TN.
- Richardson, W.S., T.B. Hudson, J.G. Wood and C.R. Phillips, 1989, "Characterization and Washing Studies on Radionuclide Contaminated Soils, in Superfund '89, Proceedings of the 10th National Conference, Hazardous Materials Control Research Institute, pp. 198-201.