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Soil Treatment To Remove Uranium And Related Mixed Radioactive Contaminants

Final Report
September 1992 - October 1995

July 1996

Work Performed Under Contract No.: DE-FC21-92MC28245

MASTER

For

U.S. Department of Energy
Office of Environmental Management
Office of Technology Development
Washington, DC

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Atomic Energy of Canada Limited
Chalk River Laboratories
Chalk River, Ontario
Canada KOJ IJO

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Morgantown, West Virginia 26507-0880

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ABSTRACT

A research and development project to remove uranium and related radioactive contaminants from soil by an ultrasonically-aided chemical leaching process began in 1993. The project was cost-shared between Atomic Energy of Canada Limited and the United States Department of Energy through the Morgantown Energy Technology Center. The project objective was to develop and design, on the basis of bench-scale and pilot-scale experimental studies, a cost-effective soil decontamination process to produce a treated soil containing less than 35 pCi/g.

The project, to cover a period of about thirty months, was designed to include bench-scale and pilot-scale studies to remove primarily uranium from the Incinerator Area soil, at Fernald, Ohio, as well as strontium-90 and selected gamma emitters from a Chalk River soil, at the Chalk River Laboratories, Ontario. The project goal was to develop, design and cost estimate, on the basis of bench-scale and pilot-scale ex-situ soil treatment studies, a process to remove radionuclides from the soils to a residual level of 35 pCi/g of soil or less, and to provide a dischargeable water effluent as a result of soil leaching and a concentrate that can be recovered for reuse or solidified as a waste for disposal. In addition, a supplementary goal was to test the effectiveness of in-situ soil treatment through a field study using the Chalk River soil.

Analysis of the ex-situ soil treatment results showed that soil pre-concentration through flotation using chelating agents was not technically viable for the Fernald Incinerator Area and the Chalk River soils. Direct decontamination of the soils through chemical leaching with dilute mineral acids in the presence of an ultrasonic field was found to meet the residual target values. The subsequent recovery of the contaminants from the soil leachate by precipitation and sorption was achieved efficiently in an ultrasonic field.

For the Fernald Incinerator Area soil, the use of dilute sulphuric acid at an optimum oxidation potential gave superior soil decontamination performance to leaching with a carbonate/bicarbonate solution. The recovered uranium as sodium diuranate from soil leaching can be reused in uranium milling plants. Similarly, the use of dilute hydrochloric acid was effective to remove short-lived isotopes (^{90}Sr, ^{60}Co and ^{137}Cs) from the Chalk River soil. The recovered secondary waste, having little value for reuse, was solidified in a cementitious matrix for disposal as low-level radioactive waste.

Depending on the soil characteristics, the pilot-scale ex-situ soil treatment tests revealed that the combined effects of chemical leachant, and thermal and flow fields employed can mask the microscopic mixing effects due to ultrasonic fields. Decoupling of these effects was not fully achieved in the present study because of the relatively fine particle size of the untreated soil and the consequent inability to sustain low flowrates of soil-water suspension to the ultrasonic cell. However, controlled soil leaching and leachate treatment experiments indicated that the use of an ultrasonic field in combination with the appropriate concentration

of chemicals and reaction temperature removed the majority of the contaminants in extremely short contact times of a few seconds. The slow contaminant removal kinetics prevalent in the zone after the majority of the contaminants are removed, was found to be best achieved in the relatively slow solid-liquid separation step involving precoat filtration equipment.

On the basis of the ex-situ soil treatment results, an integrated ex-situ soil leaching and leachate treatment plant was designed to decontaminate soil at a rate of 20 tons per hour. The flowsheet consisted of several process steps including ultrasonically-aided soil leaching, ultrasonically-aided precipitation/sorption of contaminants from the soil leachate, solid-liquid separation step involving precoat filtration equipment. A post-treatment of the water effluent resulting from the plant would be required to control specific secondary contaminants such as sulphate and total dissolved solids to suitable discharge levels.

A preliminary cost estimation of a 20 ton/hour integrated ex-situ uranium soil treatment plant was prepared. The combined cost of soil leaching and leachate treatment was estimated to be about $340 per ton of soil treated. The estimated cost included all operating costs and costs associated with capital depreciation for a plant life of 5 years. The cost estimate also assumed the reuse of the recovered uranium from the soil treatment in an existing uranium milling operation in Canada.

The limited field study involving in-situ leaching of the Chalk River soil confirmed favourably with the results obtained from bench-scale soil column leaching and pilot-scale ex-situ soil leaching test results. The field test was successful in demonstrating that strontium-90 contained in sandy soils can be mobilized easily using dilute mineral acid as leachant. The study demonstrated the utility and practicality of decontaminating aquifers containing strontium-90.

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LIST OF ACRONYMS AND ABBREVIATIONS

AECL	Atomic Energy of Canada Limited
Bq	Becquerel one disintegration per second, equal to 27 picocuries
CBD	A Leachant Formulation Consisting of Sodium Salts of Citrate-Bicarbonate-Dithionite
CFM	Cubic feet per minute
Chalk River Soil or Chalk River Chemical Pit Soil	A contaminated soil from a site called "The Chemical Pit" within the premises of Chalk River Laboratories, Ontario, Canada
CRL	Chalk River Laboratories, Chalk River, Ontario, Canada
DOE	U.S. Department of Energy
DNC	Delayed Neutron Counting
emf	Solution Electromotive force with reference to Ag/AgCl/4 mol/L KCl Saturated with AgCl at 25 °C (Reference Electrode Potential is 199 mV as measured against SHE), Eh (mV) = emf + 199
Eh	Potential of an electrode measured with SHE as reference electrode
EPA	U.S. Environmental Protection Agency
EX-SITU	Refers to the treatment of soil or soil leachate in above ground facilities. The contaminated soil is excavated and treated through chemical addition and/or other contaminant removal methods (for example, ultrasonically-aided systems). The treated soil is recovered after dewatering and returned to its original location. The soil leachate is further treated by chemical addition to concentrate the contaminants. The rate of contaminant removal is enhanced by the use of an ultrasonic field. The suspension is dewatered and the contaminant is recovered as a wet cake for either reuse as a resource or for final disposal as waste.

FEMP	. . . . Fernald Environmental Management Project
Fernald Soil or Fernald Incinerator Area Soil	A contaminated soil from the Incinerator Area in Fernald, Ohio, USA
FSQI	Feed Soil Quality Index, Defined in Section 4.3.2
FWQI	. . . . Feed Water Quality Index, Defined in Section 4.3.2
IA	Incinerator Area Soil in Fernald Site, Fernald, Ohio, USA
ICPS	Inductively Coupled Plasma Spectrometry
ICRP	International Commission on Radiological Protection
ID	Internal diameter
IN-SITU	In-situ soil remediation involves fluid injection through wells into subsurface soils. The fluid may contain water, leachant, and oxidizing and reducing chemicals. The contaminants dissolve in the fluid and then migrate to a leachate collection or production well for removal and handling through additional treatment of the leachate by ex-situ methods.
LANL	. . . . Los Alamos National Laboratory
MAC	Maximum Allowable Concentration
MDL	Method Detection Limit
METC	Morgantown Energy Technology Center, Morgantown, West Virginia
NAA	Neutron Activation Analysis
NEPA	. . . . National Environmental Protection Act
NORM	Naturally Occurring Radioactive Material
ORNL	Oak Ridge National Laboratory

ORP	Oxidation-Reduction Potential, used in the same sense as emf
PCRE	Percent Contaminant Removal Efficiency, defined in section 4.3.2
PWQI	Produced (or Treated) Water Quality Index, defined in Section 4.3.2
PRDA	Program Research and Development Announcement
QAP	Quality Assurance Plan
SDL	Sample Detection Limit
SHE	Standard Hydrogen Electrode. By convention, its potential is zero
SPA	Storage Pad Area in Fernald Site, Fernald, Ohio, USA
SRC	Saskatchewan Research Council, Saskatoon, Canada
TDS	Total Dissolved Solids
TP	Test Plan
TSQI	Treated Soil Quality Index, defined in Section 4.3.2
USDOE	United States Department of Energy
USEPA	United States Environmental Protection Agency
USNRC	United States Nuclear Regulatory Commission
WL	Whiteshell Laboratories, AECL, Pinawa, Manitoba, Canada
WTC	Waste Treatment Centre, located at AECL Chalk River Laboratories, Chalk River, Ontario, Canada

EXECUTIVE SUMMARY

SCOPE

A research and development project to remove uranium and related mixed radioactive contaminants from soils by ex-situ and in-situ treatment processes began in 1993 January as a cost-shared Cooperative Agreement between the United States Department of Energy through the Morgantown Energy Technology Center and Atomic Energy of Canada Limited. The project, to cover originally a period of twenty-four months, and later extended to thirty months, was designed to include bench-scale and pilot-scale studies to remove primarily uranium from the Fernald Incinerator Area soil, Fernald, Ohio and strontium-90 from AECL Chalk River Chemical Pit soil, Chalk River Laboratories, Ontario. The goal was to remove radionuclides from the soils to a residual level of 35 pCi/g of soil or less, to provide a dischargeable water effluent resulting from soil leaching and leachate treatment and to recover a concentrate for reuse or disposal. The target value of 35 pCi/g of treated soil corresponds to one of the values recommended by the Soil Decontamination Task Group based on risk considerations for uranium soil clean up [ORNL, 1993a; LANL, 1994]. Similar values have also been applied to the management of uranium mine tailings [Raicevic et al., 1979].

The report presents experimental and analysis results obtained from bench-scale and pilot-scale ex-situ soil leaching, bench-scale soil column leaching and in-situ leaching studies, and leachate treatment studies with and without an ultrasonic field to enhance the rate of contaminant removal.

APPROACH

The study involved a number of alternative techniques to ensure an effective removal of uranium and short-lived fission products from contaminated soils could be accomplished. At the same time, the proposed techniques are likely to remove other heavy metals that might also be present. The work provides an integrated sequence of processes to remove contaminants, primarily radionuclides of long half-life (e.g., uranium) and short half-life (e.g., ^{90}Sr and ^{60}Co) and their subsequent extraction from the leachates. The technology permits the water used in the soil leaching to be released to the environment. The concentrated uranium can be recycled in uranium milling operations, or immobilized for disposal, whereas the concentrated ^{90}Sr waste is immobilized in a cementitious wasteform for disposal.

The experimental and analysis work contained two parts. First, ex-situ soil leaching and leachate treatment were demonstrated on bench-scale and pilot-scale equipment to remove and concentrate contaminants using chemical reagents in the presence of ultrasonic, flow and thermal fields. Second, in-situ soil leaching was attempted through a field study in a test section containing sandy soils located on the premises of the AECL Chalk River Laboratories.

To facilitate the in-situ soil leaching tests, preliminary tests were also performed with bench-scale soil columns. The ex-situ and in-situ modes of soil treatments were carried forward throughout the technology development program.

The ex-situ process involved an evaluation of the use of selective flotation to remove uranium from the soil, then leaching the float fraction in an ultrasonic field in combination with chemical leachants. The contaminants can, once segregated from the soil as leachate solution, undergo size enlargement by precipitation, co-precipitation, or sorption processes to permit their removal with filterpressing equipment. The end state of the process treatment is to achieve a small volume of contaminants as wet cake suitable for immobilization, or recovery, if there is sufficient economic justification. The treated water is further processed to control the total dissolved solids as necessary and then discharged.

The in-situ process involved the injection of a suitable leachant into a known contaminated aquifer at a site at the AECL Chalk River Laboratories. Prior to performing any injections, a suitable leachant was selected based on its performance on both batch samples and soil columns to extract the contaminants. The appropriate placement of the production (collection) well adjacent to the injection well permitted collection of the contaminants as soil leachate solution. The leachate then underwent the same process as the ex-situ leachate treatment to extract and concentrate the dissolved contaminants.

The effectiveness of the treatment steps was assessed by establishing guidelines for "clean soil" quality (e.g., 35 pCi U/g for Fernald soil and 35 pCi/g of soil for combined beta and gamma emitters in the Chalk River soil) and by comparing the levels of specific contaminants in the treated soil with these guidelines. Similarly, "clean water" quality of the treated soil leachate was evaluated with reference to allowable concentrations of specific contaminants in the drinking water to compare the relative treatment performances. The recommended ICRP limits for selected radionuclides in water were also used as criteria for assessing leachate treatment performance. The results were analyzed and interpreted in terms of treatment performance factors including: 1) Treated Soil Quality Index (TSQI), 2) Produced Water Quality Index (PWQI), 3) Percent Contaminant Removal Efficiency (PCRE) and 4) Volume Reduction Factor (VRF).

EXPERIMENTAL

Bench-Scale Ex-Situ Soil Treatment

The bench-scale study involved soil preconcentration by flotation, ultrasonically-aided soil leaching and leachate treatment studies. The contaminant removal performance was established for several process variables. They included: type of mixing, type of leachant and precipitant, chemical conditioning time and temperature, ultrasonic mixing and mechanical agitation power input values, oxidising/reducing potential, and solution pH.

The soil flotation was performed with laboratory Denver flotation cell using a variety of chelating collectors and frothing chemicals. Soil leaching and leachate processing were conducted under batch and circulation mixing conditions. The batch mixing was achieved with ultrasonic horns (20 kHz and 30 kHz frequency) or mechanical agitation (stirrer speeds of 200 and 600 rpm). The circulation mixing was introduced by the combined action of the pump flow and ultrasonic mixing fields in a flow-through cell. The separation of solids (treated soil or secondary waste solids from precipitation of contaminants in the leachate) was carried out through suspension filtration in a microfiltration cell fitted with 0.2 micrometer pore-diameter membrane that was operated under pressure and/or with a Buchner filter assembly fitted with a Whatman #3 filter paper.

Bench-Scale Soil Column Leaching

The bench-scale soil columns (4.7-cm dia. by 15-cm long) consisted of stainless steel columns fitted with leachant injection and collection ports. Column endcaps were fabricated from polyethylene, using O-rings to seal against the outer surface of the column and machined inner surface with radial and concentric groves to aid uniform flow of solution. The provision of three-way valves allowed for the addition and removal of leach solutions and for manometer connections to monitor hydraulic gradients. A tubing pump supplied water or leachant to the bottom of the column at a constant rate during conditioning and leaching of the soil column.

The column leaching experiments were performed in three separate columns packed with the Chalk River soil (about 400 g per column) using 0.1 mol/L HCl, with or without sodium dithionite as the reducing agent at 5 °C and 25 °C. The leachant or water flowrate to the columns varied in the range of 17 to 42 mL/h. The column pore volume was approximately 100 mL. The porosity and column dispersivity values ranged from 0.39 to 0.42, and from 8 cm to 11.9 cm, respectively.

In-Situ Soil Leaching

The in-situ soil leaching tests were performed in a test section located at the Chemical Pit Site within the premises of the AECL Chalk River Laboratories. The site selection was partly to facilitate equipment access, and partly because of aquifer geometry and the distribution of contamination. At the experimental site, the contaminated aquifer extended from ground surface to a depth of about 3 m, and consisted of 0.10 to 0.15 m of organic soil over sand. A clayey silt stratum of 0.5 to 1.0 m thick was below the sand, and represented the lower boundary of the contamination zone. The water table was about 5 cm above the ground surface at the time of the test. The site was prepared by clearing a region of about 8 m^2 of vegetation and removing about 0.1 m of the organic soil.

For the in-situ soil leaching, a test section (3.7-m long, 0.9-m wide and 3-m deep) of the contaminated aquifer was isolated. The leachant injection and withdrawal wells were 5-cm diameter stainless steel pipes. The injection well was screened from 0.61 to 2.44 m below grade. The withdrawal well consisted of a 3.05 m screen, starting at grade without any seal around it. Multilevel samplers and piezometers were installed through appropriate casing. The pore volume of the test cell was approximately 4100 L. The solution injection to the test section followed sequential additions of different solutions at an average flow rate of 570 mL/min. The solution injections included: a) 1.34 pore volumes of sodium dithionite solution at an average concentration of 930 mg/L; b) 3.4 pore volumes of 0.1 mol/L HCl; and c) 1.97 pore volumes of water.

Pilot-Scale Ex-Situ Soil Treatment

Pilot-scale ex-situ soil treatment (soil leaching and leachate treatment) tests were performed using an ultrasonic tank (40 kHz) or tubular ultrasonic liquid processor (30 kHz) in a continuous once-through mode through the mixing cavity or in a continuous closed-loop recirculation mode through the mixing cavity and the feed head tank. The soil-solution suspension and the contaminant precipitate-solution suspension were dewatered generally with a Perrin filter press. The recirculation mode was used to achieve long contact times, while the once-through mode was used for short contact time tests. The untreated soil-water suspension flow rate was varied in the range of 5 to 40 L/min. The leachate feed for precipitation/sorption tests was varied in the range of 5 to 10 L/min. Additions of key chemicals to the experiments were made in-line for the once-through mode tests. Generally, for tests involving recirculation of the soil suspension, the required chemicals were added directly to the feed head tank.

A typical soil leaching test involved about 30 kg of untreated soil and a soil to solution ratio of 1 to 10 (w/v). Similarly, the leachate treatment tests consisted of batches of 400 to 800 L of leachates. During soil leaching and leachate treatment tests, a number of process parameters were measured and controlled. They included: untreated soil particle size distribution, soil to liquid ratio, solution pH and Eh, temperature, suspension flow rate, conditioning time, ultrasonic power input, weight of treated soil and secondary waste, and moisture content in the treated soil and in the secondary waste.

Soil and solution samples were analyzed for different metals, radionuclides and total dissolved solids (TDS). For the Fernald Incinerator Area soil, the samples were analyzed for Al, Ca, Fe, Mn, Pb, U and TDS. Similarly, for the Chalk River Chemical Pit soil, the samples were analyzed for ^{90}Sr, ^{60}Co, ^{106} Ru, ^{137}Cs, U, Ca, Fe and TDS. Uranium in soil samples were generally measured by delayed neutron counting. Solution samples containing small amounts of uranium were measured using the laser fluorescence method. Radionuclides in soil and solution samples were determined using beta scintillation counting, gamma spectrometry and Cerenkov methods. Nitric acid digested soil samples and solution samples were analyzed for metals by Inductively Coupled Plasma Spectrometry. The sulphate in the solution samples was determined by ion chromatography. A gravimetric method was employed for TDS determination in solution samples. A Fourier Atomic Absorption method was used for low concentration lead analysis.

Experimental errors associated with chemical and radiochemical analysis, experiment duplication, and sample heterogeneity were determined.

A detailed Test/Quality Assurance Plan was implemented in the project, particularly for the experimental method, process measurement, sampling and chemical/radiochemical analysis, and error estimation. Wherever possible, standard ASTM and USEPA procedures were adopted. Where reference methods were not readily available, in-house methods were used.

SOIL TREATMENT PERFORMANCE

The untreated soil had a wide distribution of contaminants, which was primarily due to sampling heterogeneity and the batch of feedstock. For example, the Fernald Incinerator Area soil gave uranium values in the range of 472 mg/kg to 672 mg/kg of soil, with 1-sigma (s) value ranging from 28 to 76 mg U/kg, depending on the test campaign.

The Chalk River Chemical Pit soil had a wide spread in the contaminant concentration. In bench-scale ex-situ soil leaching tests, the concentration of the primary contaminant, strontium-90, ranged from 899 to 1525 pCi/g of soil with an average concentration of 1204 pCi/g and s = 234 pCi/g), whereas in the soil column tests the average strontium-90 concentration was about 216 pCi/g (s = 54 pCi/g); 260 pCi/g in-situ soil leaching tests; and 512 pCi/g (s = 36 pCi/g) in pilot-scale ex-situ soil leaching tests.

Fernald Incinerator Area Soil and Leachate Treatment

Soil Treatment

Bench-scale preconcentration of the Fernald and Chalk River soils by selective flotation was not found to be technically viable for several reasons: a) the contaminant concentration in the soil was low and also its distribution was relatively uniform in the soil; b) in the case of Fernald Incinerator Area soil, uranium was mainly associated with the fines and clay fractions of the soil; c) the use of a chelating collector such as cupferron produced some promising results in the preconcentration of uranium from the Fernald soil (about 72% of the uranium was concentrated in 42% of the soil mass). Although it was recognized that a detailed examination of cupferron in the selective flotation process, which was beyond the scope of the present project, was needed, and therefore the process was not pursued further.

Bench-scale soil decontamination through chemical leaching with alkali, chelating and acidic leachants in the presence of an ultrasonic field showed that mineral acid was the most effective for removing contaminants to the target value of less than 35 pCi/g of treated soil. For the Fernald soil, a leachant consisting of 0.5 mol/L sulphuric acid with up to 0.03 g of potassium permanganate per gram of soil in two leaching stages at a reaction temperature of about 50 °C and contact time of about 1 to 3 minutes was sufficient to meet the target. A single leaching stage under these conditions produced a treated soil quality about 30% higher than the target value of 35 pCi U/g of treated soil.

Pilot-scale, ex-situ mode Fernald soil leaching tests showed that a single-stage leaching based on 0.25 mol/L H_2SO_4 and 0.03 g $KMnO_4$/g of soil with long contact times (greater than 80 min) at 40 °C, with or without ultrasonic field combined with flow mixing due to slurry pumping, was sufficient to decontaminate the soil to less than 35 pCi U/g of soil. However, the majority of uranium, over 75%, was removed at extremely short contact times of about a second by ultrasonically-aided (30 kHz frequency and 713 W power input) leaching of the soil. To meet the overall target soil quality, the use of an ultrasonic field may best be utilized in the initial reaction domain involving very low reaction times.

Fernald soil leaching with sodium bicarbonate/carbonate solution in the presence or absence of ultrasonic mixing was not sufficient to reduce the uranium level to meet the target. Although not verified experimentally, the use of an oxidising agent along with alkaline leaching may prove to be attractive, especially when the volume of final secondary waste produced by the overall process is factored in the process evaluation.

Leachate Treatment

Bench-scale and pilot-scale results showed that acidic leachates generated from Fernald soil leaching were treated effectively through ultrasonically-aided precipitation/sorption using NaOH-H_2O_2 precipitant with small amounts of Fe^{+3} addition at room temperature with extremely short contact times. The results showed that the uranium concentration in the treated water was reduced to meet target values that met the ICRP limit of 0.29 mg U/L to the drinking water limit of 0.06 mg U/L of treated water. Precipitation with lime, instead of NaOH, was also equally effective, but the disadvantage was that the amount of secondary waste produced was about five times greater than the caustic-based treatment. Evidently, the addition of lime resulted in reducing the total dissolved solids (TDS) in the final water effluent to about 2000 mg/L, which was about 10% of the TDS value in the effluent produced from NaOH treatment.

The application of a low frequency (30 kHz) and low power input (700 W) ultrasonic field in a tubular cavity was adequate to precipitate/sorb uranium and related metals from acidic solutions at alkaline conditions using extremely low contact times of a few seconds.

In the leachate generated from soil leaching with sulphuric acid, sulphate ion was the main contributor to the total dissolved solids in the treated water. To meet discharge criteria for sulphate, the treated effluent would require additional post treatment. One option would be to discharge the effluent via a sewage treatment plant based on biological activated sludge process. Another option would be to add on the proven bacterial sulphate reduction technology as a finishing step prior to effluent discharge.

Chalk River Chemical Pit Soil and Leachate Treatment

Soil Treatment

Similar to Fernald soil leaching performance data, bench-scale soil leaching results with Chalk River soil revealed that a two-stage hydrochloric acid leaching with 0.1 mol/L HCl combined with a reducing agent (0.002 g sodium dithionite per gram of soil) at 50 °C was sufficient to remove ^{90}Sr, ^{60}Co and ^{137}Cs to the target value of 35 pCi (beta + gamma)/g of treated soil. In the absence of sodium dithionite addition, the radionuclide level in the treated soil was about 50% greater than the target value. There was no advantage of increasing the HCl concentration to 0.5 mol/L. The expectation from the bench-scale results was that on a continuous, engineering-scale plant a single-stage ultrasonically-aided soil leaching with adequate water washing should meet the target for treated soil.

The pilot-scale ex-situ leaching of Chalk River soil was limited to a soil feedstock, which was about 2.5 times lower in total radioactivity than the soil used in the bench-scale tests. The lower initial level of contaminant concentration in the soil together with the flow mixing effects in continuous delivery of the soil-solution mixture in pilot-scale leaching resulted in the removal of beta and gamma emitters to meet the 35 pCi/g target using 0.15 mol/L HCl in a single leaching stage with long contact times (about 60 min) at room temperature. The effect of ultrasonic mixing in the context of soil leaching with long contact times was not evident. The use of extremely short contact times (about 4 to 5 seconds) in once-through ultrasonically-aided leaching tests gave a treated soil with contaminant concentrations of about three times higher than the target value.

The surprising results from bench-scale and pilot-scale tests were that the Chalk River soil leaching with water alone in the presence of an ultrasonic field at 5 to 10 seconds contact time removed 40 to 48% of the ^{90}Sr, originally present in the soil. This magnitude of removal was possible only with an ultrasonic field present, suggesting that leachant addition even at low concentrations was sufficient to mask the ultrasonic effects on contaminant removal from this sandy soil.

The selection of HCl as the leachant from bench-scale soil leaching study was applied to soil column leaching tests, where the untreated soil had five times lower initial radioactivity than the soil activity in the bench-scale leaching tests. As expected, over 90% of ^{90}Sr and 50% of

^{60}Co were removed in the soil column leaching with a 0.1 mol/L HCl solution. Similar removal results were also obtained when the soil leaching was performed with 0.0045 mol/L (770 mg/L) sodium dithionite solution. The only difference between sodium dithionite and HCl leaching was that the addition of sodium dithionite resulted in a large release of iron contained in the soil, the peak point of release coincided approximately with the peak concentration of ^{90}Sr in the leachate leaving the soil column. The contaminant removal efficiencies gave a treated soil quality of about 8 pCi of combined ^{90}Sr and ^{60}Co per gram of treated soil. The soil column study also demonstrated that a leachant volume of 3 to 4 pore volumes (soil bed volume) was adequate to leach essentially all radiostrontium and cobalt from the Chalk River soils.

The limited results obtained from in-situ soil leaching field study using 0.005 mol/L sodium dithionite, followed by 0.1 mol/L HCl and water washing verified the soil column leaching tests in showing that over 90% of the ^{90}Sr was removed in the test cell at the prevalent fall temperatures of 5 to 10 °C. The average concentration of radionuclide contamination was reduced from 258 pCi ^{90}Sr/g to 27 pCi ^{90}Sr/g of soil. Because of the low concentration of ^{60}Co in the initial soil, its removal efficiency could not be determined reliably.

The in-situ soil leaching under field conditions was successful in demonstrating the utility and practicality of decontaminating aquifers containing ^{90}Sr from sandy soils.

Leachate Treatment

As ^{90}Sr was the dominant contaminant in the Chalk River soil leachate, the treatment approach was to coprecipitate Sr as $SrCO_3$ along with $CaCO_3$ by the addition of lime and soda at an alkaline pH. Bench-scale treatment of HCl-based acidic leachate with lime and soda in the presence of an ultrasonic field was effective for ^{90}Sr removal. The addition of small amounts of a cation-exchange natural zeolite powder in the carbonate co-precipitation step had beneficial effects in further reducing ^{90}Sr in the treated leachate. The majority of the treated leachate results readily met the maximum allowable concentration for ^{90}Sr, gross gamma and uranium as given by ICRP [1977]. However, the stringent U.S. drinking water limit of 9.5 pCi/L for ^{90}Sr was not met by a single-stage treatment step. Indications were that a two-stage treatment would be required to meet the drinking water criterion for ^{90}Sr. The total dissolved solids (TDS) in the treated leachate was in the order of 21,000 mg/L. In addition to the presence of chloride ion, the other major contributor to the TDS was sodium ions resulting from soda. Use of CO_2 instead of Na_2CO_3 would be beneficial to appreciably reduce the TDS levels in the effluent.

On the basis of the bench-scale results, pilot-scale leachate treatment tests using a single-stage ultrasonically-aided chemical precipitation step showed that ^{90}Sr can be removed at long reactions times (greater than 60 min) to meet the ICRP limit of 270 pCi ^{90}Sr/L. A two-stage treatment would be necessary to meet the drinking water limit of 9.5 pCi ^{90}Sr/L of treated water. Since a lower leachant concentration was employed in the pilot-scale soil leaching, the TDS values in the treated leachate after precipitation/sorption of contaminants from the leachate were also low (4000 to 4500 mg/L). As with Fernald soil-leachate treatment results, ultrasonically-aided precipitation using short contact times (a few seconds) was found to be sufficient to give similar removal efficiencies (greater than 99%) for ^{90}Sr and gross gamma.

SECONDARY WASTE MANAGEMENT

The contaminants separated as wet cake from the leachate treatment step (after soil leaching is completed) constitute the secondary waste. There is much incentive to devise a cost-effective option to deal with the secondary waste. In some instances, the recovered contaminant contained in the waste can be reused as a resource. In other instances, it has to be handled as a waste and processed further to produce a stable wasteform through appropriate solidification steps prior to disposal.

The amount of secondary waste produced from the leachate treatment step is dependent on the type of precipitation reagent(s) employed. For the Fernald soil leaching with sulphuric acid, the leachate treatment produced a secondary waste containing 0.1% to 1.0% (w/w) uranium. Since the waste contained only uranium, this was a suitable candidate for reuse in a uranium mill. Furthermore, the uranium content of the ore processed in a uranium mill is comparable to the uranium content in the secondary waste. Among the precipitants tested, the application of NaOH with H_2O_2 and a flocculant based on Fe^{3+} produced as low as 70 pounds of dry secondary waste per ton of soil treated or 175 pounds of wet cake at 60% moisture per ton of soil treated. Indications were that the mass of secondary waste produced as wet cake from carbonate/bicarbonate leachate would be as low as 18 pounds per ton of soil treated. However, the apparent benefit of having small amounts of secondary waste is offset by other issues: a) the uranium removal results from the present and past studies on carbonate leaching of Fernald Incinerator Area soil have not met the target quality for treated soil; b) the recovery of uranium from the alkali leachate is not as complete as that from acidic leachate; and c) significant problems exist in the dewatering of the soil-carbonate solution slurry.

The secondary waste generated from the Chalk River leachate treatment consisted of precipitates of metals and radionuclides primarily present as carbonate and hydroxide compounds, and sorbents bearing adsorbed contaminants. For the soda-lime precipitation process, the amount of secondary waste generated was found to be dependent on the amount of lime added to the treatment to achieve the desired removal target. The results showed that the weight of secondary waste was 5 to 10 percent of the weight of the soil treated on dry weight basis. For a ton of soil treated the secondary waste amounted to 100 to 180 pounds depending on the treatment condition. The residual strontium-90 concentration in the treated water for these test results was about 265 pCi/L. The total radioactivity in the secondary waste varied from 2 to 4 microcuries per pound of dry secondary waste. The secondary waste can be stabilized in Portland cement for later placement in a licensed disposal facility.

INTEGRATED SOIL TREATMENT

An integrated soil treatment approach combines a soil leaching step with a leachate treatment step. The soil leaching is carried out either in-situ (below ground) or ex-situ (above ground) modes of operation. The leachate treatment is performed through an ex-situ mode operation. In the ex-situ mode, soil leaching is achieved with chemical leachants in the presence of an ultrasonically-aided micromixing of the soil-solution suspension, combined with macromixing provided by flow mixing. The soil suspension is then dewatered by filter pressing. The separated leachate from the treated soil is further treated using the ultrasonically-aided precipitation/sorption method to remove and concentrate the contaminants.

The suspension is dewatered in a filter press or a rotary drum filter with the addition of filter-aid materials as required. The treated leachate is further processed to control the total dissolved solids in the final effluent prior to discharge. The separated contaminant precipitate as wet cake forms the secondary waste, which is either reused (as in the case of uranium wet cake in Fernald soil treatment), or disposed of after stabilization in a cementitious wasteform (as in the case of short-lived fission products produced as wet cake from Chalk River soil treatment). The treated soil that meets the target quality of 35 pCi/g or less is returned to its origin as backfill material.

For in-situ soil leaching, the required volume of leachant (e.g., multiple porevolumes of the soil bed to be treated) is injected through a series of wells located optimally on the basis of contaminant and hydraulic conductivity distributions in the soil. The mobilized contaminants in the solution is collected through one or more production wells and pumped to the above ground leachate treatment facility. The treatment of the leachate follows the same steps as ex-situ leachate treatment described previously.

EX-SITU SOIL TREATMENT ECONOMICS

An assessment of the integrated ex-situ soil treatment economics was made by estimating the capital and operating costs of a uranium contaminated soil treatment plant with a capacity of 20 short tons per hour throughput. The soil treatment plant process included soil decontamination by ultrasonically-aided chemical leaching and treatment of the leachate by an ultrasonically-aided chemical precipitation/sorption process. The plant capital cost included costs of equipment, materials and labour involved in the installation of the complete facility. The site related cost such as building, yard improvement and plant start-up were included as fixed capital costs. A plant life of five years was assumed. The plant operating cost included labour, materials, utilities, analytical services, depreciation, taxes, insurance and plant overhead. The operating cost also included secondary waste disposal costs for on-site storage, transportation and reuse of the secondary waste in a uranium milling operation.

The capital cost of the integrated plant was $19 million and the annual operating cost was $48 million. The operating cost translated to a unit soil treatment cost of $334 per short ton of uranium soil treated. The preliminary cost analysis also showed that within the cost estimation error of ±30%, the overall treatment cost of $320 per ton of soil treated may be comparable to the cost for direct disposal of the soil without treatment. The advantages and disadvantages of these options would require further socio-economic considerations through a detailed study.

APPLICABILITY

The ex-situ, integrated soil treatment process could be considered as a stand-alone technology with the addition of suitable material handling technology at the front-end and secondary waste solidification technology at the back-end. The key components of the proposed technology is sufficiently generic that they offer flexibility to adapt a broad range of heavy metals and radionuclides present in soils. The exploitation of efficient contaminant removal methods including ultrasonic leaching and precipitation are expected to be economically attractive for ex-situ applications. The process is amenable to mobile operation, which can be taken from site to site. Through appropriate selection of chemicals and optimizing the process chemistry, the contaminant removal efficiency and the amount of secondary waste produced as a result of treatment can be optimized. The application of a low frequency and low power ultrasonic field is expected to increase the removal efficiencies of refractory components and would also facilitate in the effective design of a treatment flowsheet on the basis of additional treatability tests.

In-situ soil leaching is best suited for large contaminated subsurface areas consisting of unsaturated and saturated soils. Through a suitable selection of leaching reagents, heavy metals and radionuclides can be extracted in a single step. It appears this technique is suitable for relatively high hydraulic conductivity sandy soils with easily leachable contaminants. The leachate collected from the operation can be treated above ground using the ex-situ precipitation/sorption methods to remove and concentrate the contaminants for reuse or for disposal after stabilization as required.

Depending on the specific application, the chemistry of the process can be altered easily to meet the applicable standards for clean soil and clean water suitable for discharge to the environment.

1.0 INTRODUCTION

The cooperative research and development project, "Soil Treatment to Remove Uranium and Related Mixed Radioactive Contaminants", between Morgantown Energy Technology Center (METC), United States Department of Energy (USDOE) and Atomic Energy of Canada Limited (AECL), has been performed by AECL at its Chalk River Laboratories, Ontario, Canada. The project involved development and design of physico-chemical treatment processes for the removal of uranium from Fernald Incinerator Area Soil and fission product contaminants from Chalk River Chemical Pit soil to achieve target contamination levels below 35 pCi/g of treated soil.

The experimental and analytical portions of the project involved: a) ex-situ soil leaching and leachate treatment on bench- and pilot-scale equipment; and b) in-situ soil leaching at a site within the premises of AECL's Chalk River Laboratories, Ontario. The process schemes examined for ex-situ and in-situ modes of operation in this project are shown in Figures A.1 and A.2, respectively.

The ex-situ soil treatment technology development involved an examination of the potential use of chelation-flotation, ultrasonically-aided chemical leaching in combination with cross-flow microfiltration and tubular filter-press operations to remove uranium, related radionuclides and other metals from contaminated soils.

The in-situ process adopted the majority of treatment steps described for the ex-situ process. The basic differences with the in-situ process were that the chelation-flotation step was not applicable and chemical leaching was performed by introducing suitable leachant(s) via the injection well directly into the contaminated soil mass. The leachate stream containing the contaminants of interest, generated by chemical extraction of the soil, was brought to the surface facility via production wells. The leachate stream produced was subjected to the same treatment scheme as used for the ex-situ process.

The test-work involved the use of two types of soils: 1) a uranium soil from the Incinerator Area at Fernald site, Ohio, USA and 2) a radioactive soil containing ^{90}Sr, ^{60}Co, ^{106}Ru and trace levels of actinides from the "Chemical Pit" Area at Chalk River Laboratories, Ontario, Canada. The average uranium concentration at the Fernald Incinerator Area soil is about 520 mg/kg of soil or 350 pCi U/g of soil. The average radioactivity (beta and gamma) of the Chemical Pit soil is about 1000 pCi/g of soil. The project consisted of experimental and analysis effort that has been arranged under five tasks (Figure A.3).

The effectiveness of the described processes has been assessed by establishing guidelines for "clean soil" quality (e.g. 35 pCi U/g for Fernald soil and 35 pCi $\beta\gamma$/g for Chalk River soil) and by comparing the levels of specific contaminants in the treated soil with these guidelines. Similarly, "clean water" quality of the treated soil-leachate has been evaluated with reference to allowable concentrations of specific contaminants in the drinking water or other criteria for dischargeable water.

Task 1 consisted of pre-experimental activities. They included: environmental assessment on the project for NEPA approval, selection and acquisition of contaminated soil samples, and implementation of a quality assurance program.

Bench-scale soil treatment studies were conducted under Task 2. The activities included: selection of cost-effective leachant(s), contaminant leaching kinetic studies, cost-effective chelating agent selection, determination of flotation conditions, selection of precipitation agent and processing conditions, tests to establish waste soil and leachate volume reductions, solidification/leach tests on secondary wastes, and concentrated uranium waste utilization. Task 2 concluded with a preliminary integrated flowsheet design.

Task 3 involved pilot-scale studies on specific components of the integrated process, developed in Task 2. The effectiveness of the process, together with key design parameters, was determined.

In-situ field studies were performed at the AECL Chemical Pit Site under Task 4. The goal was to determine the effectiveness of the leachant delivery to all parts of the contaminated soil block being treated, together with the leachant effectiveness to remove gamma- and beta-emitting radioisotopes.

To conclude the study, fully integrated process flowsheets for the in-situ and ex-situ soil treatments were designed and preliminary cost estimates were made in Task 5.

As detailed in the Project Test and Quality Assurance Plan, the original project duration was twenty-four months. This was extended by six months to allow for delays resulting from receiving soil samples and reviews of the Project QA/Test plan and the Phase 1 topical report.

2.0 SCOPE OF STUDY

2.1 Scope of Bench-Scale Ex-Situ Soil Leaching Study

The objective of the bench-scale study was to perform screening and optimization tests for decontamination of the Fernald and Chalk River soils. The tests focussed on the removal of uranium from Fernald soil and ^{90}Sr, gross gamma (^{60}Co, ^{106}Ru and ^{137}Cs) from the Chalk River soil. Several treatment steps including soil flotation, soil leaching, and leachate treatment were tested. Chelating collectors were used for selective flotation of contaminants from the soils. Ultrasonic fields were employed to enhance the soil leaching and leachate treatment kinetics.

The sub-goals included:

- selection of two most promising chelating agents as collectors for uranium flotation, and determination of flotation conditions;

- selection of a minimum of the two most promising leachants by performing bench-scale soil-leaching tests;

- determination of the efficacy of ultrasonically-aided soil leaching as compared with mechanically-agitated leaching;

- selection of a suitable precipitation agent from the ultrasonically-aided precipitation tests in conjunction with microfiltration of the various precipitate suspensions, using actual soil leachate solutions; and

- evaluation of secondary waste generated from leachate treatment for its potential for reuse or for conversion to a solidified waste form for storage/disposal.

2.2 Scope of Bench-Scale Soil Column Leaching Study

The purpose of the bench-scale soil column leaching study was to evaluate the soil leaching behaviour using a leachant system selected from the bench-scale ex-situ soil leaching tests. The intent was to apply the results in the design of the in-situ soil leaching tests under field conditions. The soil used in the column test was collected from the location to be used later for the in-situ testing program.

2.3 Scope of In-Situ Field Soil Leaching Study

The scope of the in-situ soil leaching study was to test a leachant protocol to evaluate its effectiveness in removing radionuclides from contaminated sands at a test section within a waste management facility known as the Chemical Pit at Chalk River Laboratories, Ontario. In addition to providing an assessment of the leaching efficacy under actual field conditions, this task (Task 4) allowed for an evaluation of the effectiveness of leachant delivery and recovery, and of the influence of natural heterogeneities on aquifer clean-up.

The subtasks included:

- preparation of the test site;

- determination of flow properties of the test cell using tritium-spiked water as tracer;

- execution of extended duration soil leaching tests (over two weeks) by in-situ chemical injection and recovery of the leachate;

- sampling and analysis of aquifer sediment cores during and after leachant injection to determine the distribution of contaminants and their removals; and

- sampling and measurement of solution pH, Eh, and concentration of iron and radionuclides in the leachate at the withdrawal well.

2.4 Scope of Pilot-scale Ex-situ Soil Leaching Study

The scope of the pilot-scale ex-situ soil leaching tests included:

- assembly of a pilot-scale facility;
- performance of continuous ultrasonic leaching tests in tubular ultrasonic cavity and/or ultrasonic tank configurations using the conditions determined by bench-scale tests;
- completion of experiments in a closed-loop to evaluate the effect of contact time and ultrasonic power on contaminant removal from the chemically treated leachate solution, at a constant temperature which was selected on the basis of bench-scale test results;
- determination of the effectiveness of contaminant removal on a pilot scale through precipitation, microfiltration of the treated leachate suspension and filter pressing of the concentrate from microfiltration; and
- establishment of process flowsheet parameters to perform a preliminary design and cost estimate for a 20 tons per hour soil treatment plant.

3.0 BACKGROUND

3.1 Soil Decontamination

Soil decontamination processes should remove contaminants effectively to produce sufficiently clean soil for release as backfill. A small fraction of concentrated contaminants should be produced which can be converted into a form that can be stabilized for disposal. In certain instances, the concentrated residues may be subjected to further processing to allow their reuse or recycle.

A variety of techniques involving physical, chemical, biological, solidification and thermal treatments have been examined in the past for specific applications to the decontamination of soils [see for example, NETAC, 1991]. The fundamental approach of these techniques is to remove the contaminants selectively and efficiently. Interestingly, a number of similar techniques are practiced by the mining, mineral processing and petroleum sectors. The terminology used to express contaminant removal by the environmental sector is defined as the recovery of valued materials in the industrial sector.

The probable difference between the two sectors lies in the concentration level of species of interest in the solid matrix, whether it be a contaminated soil or an ore body. A unique feature of any environmental treatment process requires that it meet the constraint of near complete removal of the species from the soil. As a result, although many of the established techniques such as flotation, gravity field separation, physical washing, chemical leaching, dewatering, etc. are still applicable, the removal efficiency and reliable performance of the process techniques are absolutely essential to meet the imposed targets for clean soil and water.

The key to the viability of any process for environmental applications requires innovative methods to improve established process techniques that remove contaminants selectively and efficiently. The challenge, therefore, is to have a treatment technology sufficiently generic so that it can be applied to a variety of contaminated soils. Contaminants are typically bound to the soil as: a physically adsorbed layer, an iron oxide layer and an inner silica matrix. The use of different energy fields including ultrasonic radiation, combined with chemical additions and treatment temperature can have synergistic and enhanced effects at extremely short reaction times on contaminant removal from soil and solution matrices. If complete removal of the contaminants is desired, then essentially destructive dissolution of the soil matrix, followed by contaminant recovery from the leachate may be required. Partial dissolution of the various layers can lead to different degrees of contaminant removal efficiencies as desired.

Remedial options available for the decontamination of soils can be broadly classified as in-situ techniques and ex-situ techniques. Ex-situ techniques require excavation and subsequent processing of the soil to extract contaminants. In-situ processes are applied directly within the soil without soil excavation. For example, if chemical leaching is used, then both techniques would yield leachate solutions containing contaminants that must be processed by on-site treatment facilities.

In-situ techniques have the potential to eliminate issues related to worker safety and public health risks associated with excavation, transportation, storage and handling of hazardous wastes. However, in-situ techniques have not been sufficiently established to provide high removal efficiencies for contaminants from subsurface soils. In general, in-situ techniques have the uncertainty that the level of decontamination achieved in the subsurface after treatment may not be adequate to permit release of the land for unrestricted use. In terms of economics, in-situ techniques may be cheaper than ex-situ techniques. However, it is likely that ex-situ processing can ensure nearly complete removal of contaminants and fully meet desired targets for land reuse.

Target criteria for clean soils vary from one jurisdiction to another. For example, it would seem that choosing building material standards as target for cleaned soils is reasonable. In a similar fashion to drinking water standards may be applied as reference or target for treated aqueous effluents. Presently, there are no regulations defining legal limitations for radionuclides in building materials [Melnyk and Vijayan, 1987]. However, several guidelines have been proposed in various countries. In North America this issue is addressed on an individual case basis for a specific building material. In Europe, the emphasis has been to establish a universal guideline for all building materials. In North America, radium-226 has been the key radionuclide of concern. A maximum allowable concentration of 740 Bq/kg, or 20 pCi/g of ^{226}Ra is recommended for building material produced from phosphogypsum. This figure has provided a general standard for building materials in the U.S. The US EPA has issued a standard for the clean up of contaminated soil intended for unrestricted use. Cleanup would be required if the ^{226}Ra concentration exceeded 185 Bq/kg (5 pCi/g) in the top 15 cm of soil, or 555 Bq/kg (15 pCi/g) in the soil below a depth of 15-cm. It appears that, the issue of acceptable levels of radioactivity in industrial wastes and by-products is judged on a case-by-case basis as the need for remedial action arises.

For certain radioactive heavy metals, specific target values for contaminants in soil have been recommended by the US EPA, Simpson and Weaver [1991], requiring ^{226}Ra to be less than 7.1 pCi/g and ^{230}Th to be less than 5.0 pCi/g for a location in Colorado. For a site in Texas, Grant et al. [1991], suggested a radium level of 5 to 15 pCi/g and a uranium level of less than 42 mg/kg would be considered adequate for clean soils. A study on alternative process technologies for uranium mine tailings management [Baird et al., 1981, Raicevic et al., 1979] considered 20 pCi/g as a target for radium in the treated tailings.

An examination of recent literature reveals a number of soil remediation technologies in different stages of development. For example, a summary of technology product profiles compiled by NETAC [1991], together with our unpublished review show some forty technologies currently under development for removal of contaminants. A breakdown of the technologies shows that chemical methods for soil treatment account for about 20% of the total, physical techniques about 15%, biological methods about 15%, thermal treatment about 25% and solidification techniques accounting for the final 25%. The majority of technologies (about 75%) represent ex-situ applications and only 25% account for in-situ applications. It is interesting to note that among in-situ technologies, 50% of the technologies are directed towards organic removal from soils by air, vacuum or steam stripping. The remaining in-situ technologies are accounted by solidification (30%) and biological (20%) methods.

In summary, the past and current soil remediation technologies have been directed mainly towards ex-situ processing for soil treatment. An outline of two examples of such technologies given below may have some bearing on our approach to ex-situ process development.

A recent report by Pegg et al. [1991], describes a process based on a combined soil washing and vitrification of the concentrated soil residues as the treatment for a mixed waste Storm Sewer Sediment from Oak Ridge Y-12 facility. The basis for the process is that most of the contaminants are present only on the surface of the very small soil particles. A physical washing step removes small particles while a chemical leaching step is required to ensure the removal of contaminants from large particles. The resulting volume-reduced waste is vitrified for disposal.

The Westinghouse soil washing process [Grant et al., 1991] involves chemical extraction and physical segregation to remediate a specific contaminated soil containing radium and uranium. The process system consists of an attrition scrubber to provide intimate contacting between the soil and the extractant at a high weight percent solids level. The use of a mineral jig allows a countercurrent rinse to displace the extractant from the clean solids. The chemical leaching is accomplished by ammonium bicarbonate at alkaline pH conditions. The leachate containing radium and uranium are removed by ion exchange.

Toxic heavy metals and certain radionuclides such uranium, radium and thorium contained in soils at many of the DOE sites can not be destroyed or detoxified. In some instances, they can be contained securely by engineered barriers, and in other instances, they can be treated by in-situ chemical and bacterial treatment processes. There are a number of instances (for example, STF, 1994], where the soil may have to be excavated and processed using ex-situ facilities to remove the contaminants. The contaminants removed from the soils into leachate solutions must be concentrated and then immobilized in a stable matrix for secure disposal. The final volume of the stabilized product is generally dependent upon the total solids contained in the concentrated liquids.

The uranium-contaminated soils at various DOE sites are known to have a wide range of other toxic metals such as lead, selenium, arsenic, etc. Furthermore, the soils are likely to have a wide range of carbonate mineralization. In some cases, uranium and other heavy metals are present as refractory oxides making these soils less amenable to chemical leaching. As a result, there is sufficient incentive to develop a cost-effective, integrated technology that features flexibility to adapt to various soil conditions and yet treat the waste reliably with little or no additional adverse impacts on the environment.

For the above reasons, the integrated process flowsheet developed in this project is believed to be sufficiently flexible to handle ex-situ as well as in-situ soil processing. The basic process scheme employs a number of physical and chemical techniques commonly used in the mining and petroleum sectors, but focusses on preferential enhancements to permit efficient removal of contaminants.

3.2 Rate Enhancement Effects Due to Ultrasonic Irradiation

For enhanced species transformation from solid or solution matrices, a satisfactory explanation of the effect of ultrasonic fields is not yet available. However, experimental observations show that reaction times are considerably shorter (a few seconds to a few minutes) than transformation based on macroscopic mixing provided by standard mechanical agitation. The impact of physico-chemical effects of low-frequency (20 to 100 kHz) ultrasound have been shown to dependent on the extent of ultrasonic cavitation [Mason, 1990]. The phenomenon of cavitation is essentially the formation of pressurized expansions and cavities filled with vapour or gases (dissolved in the liquid) within the liquid. When they collapse the cavities produce local shock waves and pressures which attain several tens of megapascals, and also create high local temperatures and charges. The ultrasonic vibrations produced by a generator not only cause oscillatory motion in the medium adjacent to it but also produce a continuous displacement of the medium, called the "sonic wind". The sonic wind manifests itself as a strong current which produces intensive mixing in microscopic scale in the fluid medium.

Several factors influence cavitation. They include: 1) physical properties of the solvent; 2) solvent temperature; 3) ultrasonic frequency; 4) ultrasonic irradiation power; 5) presence of dissolved gas; and, 6) presence of particles. Although some of these factors increase cavitation (a positive effect), others can influence cavitational effects adversely (negative cavitational effect). For example, increasing the reaction temperature up to the boiling point of the solvent in the presence of an ultrasonic field can result in a "negative cavitational effect". In one-half of the ultrasonic wave cycle (the rarefaction cycle), as a result of the reduced pressure generated, the solvent would boil. Any cavitational bubbles formed would fill rapidly with the solvent vapour. Collapse of these vapour-filled bubbles during the second-half of the cycle (compression cycle) would be 'cushioned' thereby reducing the extremes of temperature and pressure generated. Under these conditions, it may be possible that the bubbles would not collapse at all [Mason, 1990].

Intensive ultrasonic vibrations have a significant effect on rate processes taking place in solutions [Nosov, 1965]. They are able to disperse, coagulate and emulsify matter, precipitate dissolved ions and change the rate and character of solute dissolution and crystallization, produce chemical changes and increase significantly the rate of diffusive reactions.

3.2.1 Removal of Contaminants from Soil Matrices

Leaching of metal contaminants from soils is a well established unit operation in mineral processing. Specifically, a wide variety of chemical reagents (leachants) has been employed in the past to remove uranium and related heavy metals such as thorium and radium [Baird et al., 1981; Nirdosh et al., 1983; Hester, 1979]. Examples of typical leachants include mineral acids salts of mineral acids and alkaline chemicals (bicarbonate/carbonate mixture). The use of a particular chemical agent depends on the nature of the soil (alkaline or acidic, or refractory), its selectivity and the target yield for recovery.

In most mineral processing applications a target metal recovery, on average, of about 95% seems reasonable. However, this may not be suitable for contaminated soil treatment, where higher removals would be needed to quality assure discharge criteria for clean soils. Consequently, leaching techniques must be efficient, simple and selective, and must involve low concentrations of chemicals.

Ultrasonics combined with chemical treatment to leach specific components from solid matrices has been known for sometime, although only recently industrial applications for this technique are being pursued. For example, Vijayan et al. [1992] have shown that enhanced release rates (two to three times greater than that can be obtained by mechanical stirring) of trace levels of stimulants with removal efficiencies of 95 to 99% can be achieved using ultrasonically-aided water leaching of cocoa beans.

Soil leaching efficiency can be enhanced significantly by applying ultrasonic irradiation to soil-liquid suspensions [Canterford, 1984]. Because the forces of ultrasonic cavitation go beyond those which can be achieved by mechanical means, appreciable improvements in metal recovery can be achieved using short contact times. The use of short contact time between the soil and leachant would be expected to provide a compact treatment system, lower the energy requirements, and reduce concentration heterogeneities in the treated soil.

3.2.2 Removal of Contaminants from Solution Matrices

The mechanisms and effects of ultrasonic irradiation in conjunction with chemical addition and temperature on solute (ions or molecules) removal by precipitation and sorption processes in solutions have not been fully understood. It appears that the following effects are produced by ultrasonic fields with respect to metal removal from solution [e.g., Mason, 1990; Vasil'ev and Kuzhakova, 1969; Chendke, and Fogler, 1975]:

- Availability of reagent concentration on a microscopic scale needed for metal reaction is much higher than the bulk concentration, leading to reduced reagent consumption;

- Boundary-layer resistance (both hydrodynamic and electrostatic layer thickness) is reduced considerably there by enhancing diffusive processes;

- Cavitation caused by the ultrasonic field produces shock waves which produce very high local pressures, a state conducive to spontaneous reactions;

- Once the solid precipitates are produced, these particles are broken and dispersed in the bulk solution uniformly, which leads to increased surface charge, thus promoting increased rates of ion exchange and sorption processes; and

- In many situations, the dispersed particles are crystal-like, rigid particles and can be filtered easily by standard filtration equipment.

Some relevant findings from past investigations are summarized below.

Vasi'ev and Kuzhakova [1969] found that short exposures to ultrasound produced almost complete precipitation of a number of inorganic compounds for which a prolonged standing was required without the ultrasound for complete precipitation. Takuma [1976] claimed that in the presence of ultrasound $Al(OH)_3$ was recovered in a short time with nucleation control and good filterability. Hitachi [1982] reported that the flocculation process is enhanced when a vibrating element is suspended in a precipitation tank.

The use of ultrasonic in large-scale liquid mixing can be found in a report by Murry [1975]. Certain jet-edge homogenizers have shown significant energy savings. For example, to process a liquid throughput of 1000 gpm required 40 to 50 hp using conventional high-pressure mechanical homogenizers, while a single triple-jet-edge unit required only 7 hp.

A study [Chowdhury, 1987] reported contact times of about two minutes to achieve a reaction between iron particles and soluble copper, gold, silver, or platinum in the effluent stream using a 32 liter vibrating reactor, compared with several hours in conventional reactors, and the consumption of iron reagent was also reduced by about 60%.

A detailed study of ultrasonic-aided treatment of acidic leachates to remove metal contaminants began in 1993 through a project under a Cooperative Agreement between AECL and USEPA [AECL, 1993]. Results from bench-scale studies have shown that under suitable process chemistry conditions, most metals including Cu, Al, Zn, Mn, Mg, Pb, U, Ra and Fe can be removed efficiently within a reaction time of a few seconds to tens of seconds.

4.0 METHODOLOGY

The technology that has been developed consists of ex-situ and in-situ soil treatment processes that involve several innovative techniques. In ex-situ soil treatment, several techniques including soil flotation, ultrasonically-aided leaching and ultrasonically-aided leachate treatment by precipitation, ion-scavenging, microfiltration and filterpressing steps, are used. The in-situ soil treatment utilizes chemical leaching of the contaminated soil in the field. The expectation exists that the ex-situ technology will remove uranium from Fernald Incinerator Area soil to a residue level of less than 35 picocuries uranium per gram of treated soil. This value corresponds to levels previously established by the Nuclear Regulatory Commission for uranium mine tailings. The value is equivalent to 52 mg U/kg of soil based on secular equilibrium of the uranium isotopes (^{234}U and ^{238}U) in naturally occurring uranium [ORNL, 1993a and 1993b].

The technology was further developed using Chemical Pit soil containing several radionuclides (^{90}Sr, ^{60}Co, ^{106}Ru and ^{137}Cs) from a site at AECL Chalk River Laboratories. The process was expected to provide clean soil, dischargeable water and a concentrate that can be reused or stabilized into a suitable waste-form for disposal.

The approach taken by AECL to remove soil contaminants has a number of advantages. First, the various unit operations are straight-forward, the equipment is simple to operate, robust and compact making the processes amenable to easy field implementation. Second, with an integrated process, better quality control in processing can be achieved. For example, if the residual uranium in the soil is too high, the contaminated material can be recycled or the leachant reinjected. The same applies to the treatment of aqueous leachate obtained from stripping uranium from the soil. If the treated water is not acceptable for discharge, it can either be reused in the extraction process or recycled through the purification phase to reach the acceptable discharge criteria. Finally, the innovative application of an ultrasonic field to both soil decontamination and purification of leachates will provide a cost-effective technology not only for uranium cleanup but to a broader range of radioactive contaminants and heavy metals present in contaminated soils. The contaminants removed from the soil leachate are either recovered as a resource for reuse or stabilized into a suitable waste-form for disposal.

The effectiveness of the soil decontamination tests is assessed by establishing release guidelines for "clean soil" and "clean water". Accordingly, "clean soil" quality is assessed with reference to its deviation from acceptable levels for specific contaminants (e.g. 35 pCi/g of soil or less for uranium, and combined beta and gamma activity of 35 pCi/g or less for the treated Chalk River soil). Similarly, "clean water" quality is evaluated with reference to the drinking water limit (U.S. drinking water limit and/or ICRP limit for maximum allowable concentration) for specific contaminants. Specific target parameters to assess the process effectiveness include: 1) flotation yield and quality of tail; 2) quality of soil after leaching of contaminants; 3) produced water quality after removal of contaminants into a concentrate; and, 4) solidified/stabilized waste-form characteristics.

Results obtained from various experimental tasks were analyzed and interpreted in terms of the following target parameters defined in section 4.3.2: (a) Treated Soil Quality Index (TSQI); (b) Produced Water (or Treated Leachate) Quality Index (PWQI); (c) Percent Contaminant Removal Efficiency (PCRE); (d) Volume Reduction Factor (VRF); and (e) Leachability Index.

4.1 Facilities and Equipment

4.1.1 Bench-Scale Ex-Situ Soil and Leachate Treatment Apparatus

The ex-situ mode of soil leaching and leachate processing was conducted through chemical treatment under batch and circulation mixing conditions. The batch mixing was achieved with ultrasonic horns or mechanical agitation. The circulation mixing was achieved by the combined action of the pump flow and the ultrasonic mixing fields in a flow-through cell. The separation of solids (treated soil or secondary waste solids from precipitation of contaminants in the leachate) was carried out through suspension filtration in a microfiltration cell that was operated under pressure.

Several primary and ancillary equipment, measuring and control instruments were used in the bench-scale test study. A list of equipment and instruments is given in Tables B.1 and B.2.

4.1.2 Bench-Scale Soil Column Leaching Study

Soil columns were constructed using 4.7-cm inside diameter stainless-steel tubing in 15-cm lengths. Column endcaps were fabricated from polyethylene, using O-rings to seal against the outer surface of the columns and machined on the inner face with radial and concentric grooves to facilitate uniform flow. Omnifit three-way valves allowed for the addition and removal of leaching solutions as well as for connection to manometer tubes when monitoring hydraulic gradients. Sage Model 375A tubing pumps were used to supply water or leachant to the bottom of the columns at constant rates during conditioning and leaching of the column contents.

4.1.3 In-Situ Soil Treatment System

Site Description

The Chemical Pit site consists of two linked infiltration pits located in a fenced compound on the premises of Chalk River Laboratories Outer Area (Figure A.4). First, a circular pit was constructed in 1956 and a trapezoidal extension was added in 1959 when wastewater inputs began to exceed infiltration capacity. Between 1956 and 1993, radioactive wastewater from CRL operations was sampled and collected in a holding tank located in the CRL Inner Area and pumped to the pit via a pipeline as required.

Since 1993, this wastewater has been directed to the CRL Waste Treatment Centre (WTC), although the Chemical Pit remains as a back-up that is available for times when the WTC is unable to process the wastewater. Since commissioning, the volumes of wastewater transferred to the Chemical Pit have been recorded, along with results of analyses for ^{90}Sr, total beta-gamma, and gross alpha activity. Measurements of tritium concentrations were added in the 1960's, and since 1987 the list of reported parameters has included the predominant gamma emitters, uranium, solution pH, and electrical conductivity. Up to 1994, the decay-corrected inventory of ^{90}Sr transferred to the Chemical Pit was just over 11 TBq (297.3 Ci), and about 90% of the input ^{90}Sr inventory is still in the study area.

The region around the Chemical Pit, with the locations of subsurface monitors that have been used to delineate the contaminant plume, and the extent of groundwater contamination from the pit as defined by tritium, is shown in Figure A.4. There is diffusive discharge of groundwater to surface in the wetland, and drainage leaves the region by overland flow through East Swamp Stream. Continuous measurements of streamflow and weekly water sampling have been conducted at a weir located approximately 100 m south of the area shown in Figure A.4.

Because of limited input and output data, similar flux balances cannot be easily prepared for other isotopes, although there is a substantial spectrum of radionuclides present in the groundwater plume from the Chemical Pit. After tritium, ^{90}Sr and ^{60}Co were predominant, with almost all of the strontium present as cationic species while most of the dissolved ^{60}Co occurred as anionic complexes. Ruthenium-106 was then, and until 1993 continued to be, the third most abundant radioisotope in the Chemical Pit plume, but unlike strontium and cobalt, ruthenium has shown only very limited interactions with the aquifer sands. Although transuranics are also present in the study area groundwaters, concentrations are too low to allow for their detailed characterization during this investigation.

Details of the groundwater flow system around the Chemical Pit site can be found in a study prepared by Killey and Munch [1984]. The recharge area for the portion of the sand aquifer that underlies the infiltration pit covers an area of about 14,000 m^2 upgradient of the infiltration pit. This provides a natural groundwater flux of about 9 $L \cdot min^{-1}$ through the section of aquifer affected by the Chemical Pit. Groundwater residence times are short, and are estimated to be between 6 months and 2 years, depending on the flow path. Linear average flow velocities derived from hydraulic conductivity estimates and measured hydraulic gradients were between 0.3 and 0.5 $m\cdot d^{-1}$.

Test Cell Design and Installation

The region of aquifer adjacent to borehole ES-31 (Figure A.4) was chosen for the field test, partly to facilitate equipment access, and partly because of aquifer geometry and the distribution of contamination. At the experimental site, the contaminated aquifer extends from ground surface to a depth of approximately 3 m, and consists of 0.10 to 0.15 m of organic soil over sand (Figure A.5). A clayey silt stratum (0.5 to 1.0 m thick at the test site) underlies the sand, and represents the lower boundary of the zone of contamination. The water table in the area is normally within a few centimetres of ground surface. However, in 1994, unusually high rates of precipitation in the spring and summer led to the water table being approximately 5 cm above ground surface at the time of the test. The site was prepared by clearing a region approximately 8 m square of vegetation and removing roughly 0.1 m of the organic soil. The organic soil excavation accompanied the removal of stumps and roots.

Because of this configuration and contaminant distribution, isolation of a section of the contaminated aquifer in an impermeable cell was feasible. Mild steel plate (0.63 cm thick) was selected as the material for the cell. Construction details and the dimensions of the test cell are given in Figure A.6. The test cell, measuring 3.7-m long, 0.9-m wide and 3-m deep, was installed using a track-mounted backhoe equipped with a pneumatic hammer on the end of the boom. An inverted "U"-shaped head fabricated to fit loosely over the top rim of the test cell was attached to the pneumatic hammer.

In operation, the hammer was positioned near one corner of the box, which was then driven until the test cell had sunk about 0.1 m. The diagonal corner of the cell was then driven down until it was a few centimetres lower than the starting location. This was continued, pausing to remove the temporary internal cross-bracing as the cell sank, until the bottom of the test cell was located 3.15 m below grade, in either the clayey silt stratum or, at the south end, just into the underlying till.

At the locations for the wells, and for the multilevel piezometers, a continuous core of soil was collected using standard coring methods described in section 5.1. Screens for the injection and withdrawal wells were 5-cm inside diameter Johnson stainless-steel with a 0.025-cm slot size. The injection well was screened from 0.61 to 2.44 m below grade, with a stainless-steel riser pipe and a 0.3-m thick surface seal of Wyoming bentonite in the annular space left around the well when the casing was withdrawn.

The withdrawal well consisted of a 3.05 m screen, starting at grade, and no seal was installed around it or any of the observation wells. The multilevel piezometers were made of 1.3-cm inside diameter polyethylene tubing, with an intake screen consisting of a 7.5-cm length of fritted polyethylene (VYON) tubing, attached at the bottom using polyethylene glue. The multilevel samplers were strapped to a central 3.2-cm inside diameter Schedule 40 PVC pipe, and the bundle was then installed through a 0.06-m inside diameter casing. The PVC pipes used in the multilevel samplers, and in the single-tube monitors, were sealed at the bottom, and were used as dry access tubes for gamma logging.

A schematic of leachant injection and withdrawal arrangements for the in-situ study is shown in Figure A.7.

4.1.4 Pilot-scale Apparatus

Two series of tests using different types of ultrasonic and filtration equipment were performed for the Chemical Pit soil. The first series of experiments (Figure A.8) employed an ultrasonic tank for soil leaching and a frame-and-plate Perrin filter press to separate the treated soil from the leachate. The soil leachate was treated by precipitation and dewatering by microfiltration and tubular filter press systems. The second series of tests (Figures A.9 and A.10) involving Fernald and Chalk River soils treatment utilized an tubular ultrasonic liquid processor for soil leaching and leachate treatments. The Perrin filter press was used for separating the treated soil from the leachate as well as the secondary waste solids from the treated water.

A summary of the primary equipment and instruments employed in the pilot-scale tests is given in Table B.3. A detailed account of equipment and components is given along with the test procedure in section 4.3.3. Photographic views of the pilot-scale ex-situ soil and leachate treatment facility are shown in Figure A.11.

4.1.5 Waste-Form Evaluation

A number of physical and chemical test methods are specified by different regulatory requirements for waste form evaluation. Some method are specified only as guidelines. The recommended physical tests include free water content, unconfined compressive strength, freeze/thaw weathering, radiation resistance, biodegradation, wet/dry weathering, hydraulic conductivity and bulk density. Chemical tests include the US EPA Toxicity Characteristic Leaching Procedure (TCLP), and acid neutralization capacity and dynamic leach test [Kasten et al., 1989; USNRC, 1991; Stegemann and Cote, 1991, and Environment Canada, 1991].

The United States Nuclear Regulatory Commission, in 10 CFR Part 61, "Licensing Requirements for Land Disposal of Radioactive Waste", established licensing procedures, performance objectives, and technical criteria for the shallow land burial of low-level radioactive waste.

As part of the criteria [USNRC, 1991] to ensure the long-term safe performance of a burial site, the waste must maintain their physical integrity for at least 300 years. Thus, the product waste form should have the following characteristics: (a) the waste should be in a solid form that provides stability after disposal; (b) the waste should not contain free standing and corrosive liquids; (c) the waste should be resistant to degradation caused by radiation; (d) the waste should be resistant to biodegradation; (e) the waste should remain stable under the compressive loads inherent in the disposal site, and (f) the waste should remain stable if exposed to moisture or water after disposal.

The USNRC [1991] technical position paper on waste form was developed based on the above criteria to provide guidance on waste form test methods and results acceptable to the USNRC staff for implementing the 10 CFR Part 61 waste form requirements.

The secondary waste generated by the Chalk River soil leaching was stabilized in cement. The unconfined compressive strength and the leachability index of the product waste form were determined by load displacement using a mechanical tensile machine, Intron Model 4206 and by dynamic leach tests, respectively. These two are the most important performance parameters of the cement-based waste form specified by the USNRC. The waste form should withstand at least 500 psi of compressive strength and should have a leachability index greater than 6 for the contaminant of interest [USNRC, 1991].

A description of equipment used in the tests is given along with the test procedure in section 4.3.3.

4.2 Reagents and Supplies

A list of chemicals employed in the test program with their sources, purity and intended use is summarized in Table B.4.

4.3 Experimental

4.3.1 Waste Influents

Fernald Incinerator Area Soil

The Fernald site in Fernald, Ohio has been the principal location for the production of purified ingot feed material for use in nuclear reactors at Savannah River and Hanford. The Fernald site, now designated under the Fernald Environmental Management Project (FEMP), consists of 1050 acres. In the uranium operation during 1950 to 1988, the manufacturing processes, which were housed in a fenced area covering approximately 136 acres, included uranium and thorium metal production, and uranium hexafluoride reduction. In 1960, the production peaked at approximately 10,000 tons of uranium and gradually declined to about 1270 tons in 1975. In the mid-1980s, production increased slightly and later in 1989 production ceased as a result of a decline in demand for uranium products.

During the production period, uranium was released from several sources on the Fernald site at various locations and in various forms. Examples of the sources include deposition of airborne-uranium particulates generated from stacks and leaks/spills of uranium containing solvents and process effluents produced from aqueous and non-aqueous processing. Indications are that soil volumes in excess of 70 million cubic feet may contain unacceptable levels of uranium.

Of the several sources for uranium contaminated soils, two areas have been and are being examined to establish a cost-effective decontamination process. These are known as the Storage Pad Area (SPA) and the Incinerator Area (IA). The Storage Pad Area appears to be contaminated by uranium product spills. The Incinerator Area seems to have been contaminated by airborne uranium material. The uranium concentration in these soils vary from 350 to 550 mg U/kg of soil.

The particle size distribution of these soils is similar. The silt and clay fraction is about 85%, the sand fraction is about 12 to 14% and about 1 to 5% is gravel. The uranium distribution is significantly different between the two soils. The silt and clay fraction contains approximately 95% U for the SPA soil and 73% U for the IA soil; the sand fraction contains about 5% U for the SPA soil and 26% for the IA soil; and less than 1% U is contained in the gravel fraction for both soils.

The uranium in the Fernald Incinerator Area soil is not distributed homogeneously throughout the soil or within the individual size fractions. For the Incinerator Area soil used in the present study, the concentrations and distributions of uranium are given in Table B.5. The Incinerator Area soil sample received from the Fernald Site was screened to remove gravel, and desired particle-size fraction was used in the bench-scale and pilot-scale tests. In bench-scale tests, the soil was treated in a ball mill to achieve uniformity of the feedstock. The particle-size distribution is given in Figure A.12.

Chalk River Chemical Pit Soil

The soil was obtained from the Chemical Pit area at a site in Chalk River Laboratories, Ontario (section 4.1.3). Cored soil samples from ES-16 and CP-4 locations (Figure A.4) were used in the bench-scale tests. Soil which was collected in the vicinity of ES-16 and CP-4 locations were used in the pilot-scale tests. The bench-scale soil column leaching and in-situ leaching tests were performed with soil at ES-31 location.

The Chemical Pit is circular and was excavated and filled with washed gravel in 1956. A trapezoidal extension was added in 1959 when the initial pit was unable to drain the waste water influent to the pit quickly enough and began to flood to the surface. Radioactive waste water from the laboratories was pumped periodically by pipeline until 1992.

The soil is contaminated with beta and gamma emitting radioisotopes. Beta activity of 900 to 1500 pCi/g of soil is primarily due to ^{90}Sr. Gamma activity of 80 to 110 pCi/g of soil is mainly due to the presence of ^{60}Co (~80%), and combined ^{106}Ru and ^{137}Cs (~20%). Even though it is only a beta emitter, ^{137}Cs contributes to gamma activity through its daughter, the metastable ^{137}Ba. The uranium concentration in the soil varies from 5 to 10 mg/kg of soil.

The particle size distribution of unground soil samples follows a pattern exhibited by a well-graded sand. The median particle diameter is 185 μm (Figure A.12) The analysis of the soil is given in Table B.6.

4.3.2 Target Parameters

Results obtained from various experimental tests were analyzed and interpreted in terms of the following target parameters.

(1) Treated Soil Quality Index (TSQI)

TSQI is defined as the ratio of the concentration a specific contaminant in the treated soil to the maximum allowable concentration of the contaminant in "clean" soil. This parameter determines the quality of the outgoing soil from the process and denotes the effectiveness of the soil decontamination process.

A value of 35 pCi or less for total radioactivity per gram of soil was used as target value for treated soil. This corresponds to 52 mg natural uranium per kilogram of treated Fernald soil and 35 pCi of combined ^{90}Sr and gross gamma per gram of treated Chalk River soil.

It should be noted that for natural uranium, the ratio of activity of ^{234}U : ^{235}U : ^{238}U is 1 : 0.046 : 1. The ratio of ^{234}U (daughter of ^{238}U) to ^{238}U is expected to be 1 at secular equilibrium, since they are in the same radioactive series. Based on the activity ratio, a conversion factor that equates 1 μg of uranium to 0.07 pCi of uranium is commonly used.

(2) Produced Water (or Treated Leachate) Quality Index (PWQI)

PWQI is defined as the ratio of the concentration of a specific contaminant in treated leachate (or produced water) to the maximum allowable concentration of the contaminant in "dischargeable" water. This parameter determines the quality of the outgoing water from the process and denotes the effectiveness of the leachate decontamination process.

For uranium in the treated water, we have used the U.S. drinking water limit of 0.06 mg/L [USEPA, 1990] and the ICRP 1977 limit of 0.29 mg/L as target values. For ^{90}Sr, we have used both the U.S. drinking water limit of 9.5 pCi/L [USEPA, 1990] and the ICRP 1977 limit of 270 pCi/L. For gross gamma in the treated water, the ICRP 1977 maximum allowable concentration of 2700 pCi/L has been employed.

(3) Percent Contaminant Removal Efficiency (PCRE)

The removal efficiency of a specific contaminant as a percentage of the feed stream (contaminated soil or soil leachate) concentration is defined as a ratio of the treated soil quality index (TSQI), or product water quality (or treated leachate quality) index (PWQI) and the feed soil quality index (FSQI) or feed water (or leachate) quality index (FWQI).

Thus:

PCRE = [1 - (TSQI / FSQI)] x 100 for soil decontamination

PCRE = [1 - (PWQI / FWQI)] x 100 for leachate treatment

where:

FSQI is defined as the ratio of the concentration of a specific contaminant in the feed soil to the maximum allowable concentration of that contaminant in "clean" soil; and

FWQI is defined as the ratio of the concentration of a specific contaminant in the leachate feed to the maximum allowable concentration of the contaminant in "dischargeable" water.

(4) Volume Reduction Factor (VRF)

The volume reduction factor is determined by the ratio: [Total feed volume] / [Final waste concentrate volume].

(5) Leachability Index

Leachability indices for the contaminants concerned in the product waste are determined using the dynamic leach test. The dynamic leach test procedure recommended by the USNRC is the American Nuclear Society Test ANSI/ANS 16.1-1986 [ANS, 1986].

The ANSI/ANS 16.1-1986 procedure allows for an accumulation of data over a period of time to serve as a basis for indexing contaminants release from solid waste form under controlled conditions. The procedure employs periodic leachant replacement to simulate the conditions of a continuous flow system. The leachant is controlled in a specified temperature range (17.5 to 27.5°C), and the leachant volume to sample geometric surface area ratio is approximately 10 cm. After initial, rapid removal of any mobile surface contamination, the early leach rates observed can be explained by the diffusion mechanism. If other mechanisms are important factors, their control is generally discernible only after longer leaching. Under the conditions specified by ANSI/ANS 16.1-1986 [ANS, 1986], mass transport equations permit the calculation of an effective diffusivity. If less than 20% of a leachable species has been removed by the time $t = \sum(\Delta t)_n$, the effective diffusivity can be calculated by the equation:

$$D = \pi \left[\frac{(a_n/A_o)}{(\Delta t)_n} \right]^2 \left[\frac{V}{S} \right]^2 T$$

In a typical flotation test, 100 grams of soil sample was wet-ground with water for 20 minutes with zirconia cylindrical grinding media. The pulp was transferred to a 1 liter flotation tank and mixed with about 200 mL water. To this mixture, a preselected amount of a chelating collector reagent was added and the mixture conditioned for about 30 minutes by mechanical agitation. At this stage, a further quantity of water and frother agent was added.

The soil was then floated by introducing air at a predetermined flow rate and the froth containing the floated material was withdrawn from the tank. The volume of the pulp in the tank was maintained by adding makeup water. When all floatable material was exhausted, the agitation and air flow were stopped.

The float and the tail (non-float) fractions were filtered separately in a Buchner funnel fitted with a Whatman #3 filter paper. The recovered soil fractions were prepared for sample analysis. All flotation tests were carried out at room temperature (20 ± 3 °C).

Ultrasonically-Aided Soil Leaching

Soil leaching studies were carried out in 1 liter glass beakers. The batch-mode ultrasonic mixing of solutions was achieved using a standard laboratory-scale Branson ultrasonic system. This system consists of a power supply and cylindrical probes equipped with a converter and a booster. Through appropriate selection of the components, the system can deliver power at 300 to 900 Watts at a frequency of 20 kHz. The ultrasonic power input to leaching was determined by measuring the line current and voltage

To suspend the soil particles uniformly in the glass vessel, a mild agitation by a magnetic stirrer was provided. The leaching temperature was maintained by placing the vessel in a constant temperature water bath. The suspension produced at the completion of leaching, specified by a fixed time for leaching, was filtered using a Buchner funnel fitted with a Whatman #3 filter paper under a slight vacuum. If the filtrate obtained was turbid, then it was filtered through a 0.2 μm pore diameter polypropylene microfilter in an Amicon membrane cell at 10 psig nitrogen pressure.

The filter cake (treated soil) was washed with water, weighed, and dried at 100 °C in an electric oven and reweighed. The dried cake was ground, mixed and split into 2 gram or 10 gram aliquots (as determined by sample analysis requirement) and analyzed for contaminants. A predetermined volume (100 mL to 200 mL) of the filtrate (leachate) was sampled to obtain chemical analysis.

In the "Recirculation" mode for the ultrasonically-aided soil leaching tests, the feed slurry was fed to a flow ultrasonic cell system at a flow rate of 3 L/min in a closed-loop. After a predetermined elapsed time (corresponding to leaching contact time), the ultrasonic power input was cut off and the resulting suspension was subjected to a solid-liquid separation step as described under the batch-mode, ultrasonically-aided soil leaching test procedure above, to obtain treated soil and leachate samples for analysis.

Mechanically-Agitated Soil Leaching

The test procedure used a Fisher agitator for mixing the soil-leachant suspension at a stirrer speed of 600 rpm. All other procedures were similar to ultrasonically-aided soil leaching. The power of agitation was determined by measuring the current and the line voltage.

Soil Leachate Treatment

For bench-scale soil leachate treatment tests, a known volume of soil leachate feed solution was mixed for a fixed time ultrasonically, either in a batch mode or recirculation mode, at a specific power, frequency and temperature with the desired chemical addition. This chemical treatment was performed in 1 liter glass beakers to precipitate and scavenge/ion exchange contaminants.

The batch-mode and recirculation mode of ultrasonic mixing of solutions were achieved by methods described previously under soil leaching. The leachate feed, together with all required chemical additives, was pumped to a flow ultrasonic cell system at a volumetric flow rate of 3 L/min in a closed-loop. After a predetermined elapse of time (corresponding to leaching contact time), the ultrasonic power input was cut off and the resulting suspension was subjected to a solid-liquid separation step involving flat-sheet microfiltration to obtain treated water samples for chemical analysis.

The chemically treated waste suspension was filtered in a membrane cell following the procedure and equipment described below. Samples of the feed solution and the filtrate were taken and analyzed for contaminants.

Filtration Equipment

Bench-scale filtration was carried out with Amicon stirred filtration cells. A membrane cell of 200 mL capacity consisted of a special flat-sheet membrane holder to allow easy insertion and removal of the membrane without damage.

The filtration pressure was maintained at about 150 kPa (10 psig) by nitrogen gas from a cylinder. The temperature of the operation was kept at room temperature (~23 ± 2°C). During filtration, the suspension was stirred by a magnetic stirrer bar that was equipped as part of the cell. The beaker design allows the test sample to be poured in and out easily, to provide maximum recovery and virtually no fluid loss.

The stirring bar configuration facilitates efficient stirring and high filtration rates. The cell has a grid type membrane support and a filtrate outlet with no support disc, which minimizes the holdup volume. A 0.2 μm nominal pore diameter flat-sheet membrane was used for microfiltration.

(b) Bench-Scale Soil Column Leaching Study

During the leaching tests, column effluents were collected in LKB fraction collectors set for fixed time intervals, to confirm flow rates.

Wet bulk sand from ES-31 was packed in nominal 1 cm layers into the four columns, tamped gently and just enough water added to saturate the soil between additions. Groundwater collected from ES-31 at a depth of 1.5 m was pumped continuously through the columns at 1 L/d for at least three days to condition them before use.

Measurements of solution pH in column effluents were made using a Beckman PHI-12 meter and a Beckman low ionic strength electrode, after two-point calibration and with checks every 20 samples (or at the end of the batch) of the pH 4 and 7 buffers. Sample pH values were measured within 24 hours of collection. Samples collected were stored in a refrigerator. Redox potentials were measured using an Orion Model 407A meter and an Orion combination platinum electrode (Orion 90-01). Iron was measured by atomic absorption spectrometry (Varian SpectrAA-10), calibrated with standards diluted from a commercial stock solution (Fisher), and with samples diluted as required to keep absorbance in the range required by the standards. A set of four standards was run after every 20 samples.

Tritiated groundwater was added after initial column conditioning to check for channelling or major heterogeneities. Tritium concentrations were measured using a 5:1 scintillation cocktail (Packard Ultima Gold) to water ratio, counting the samples (and blanks of distilled Ottawa River water) in a Packard Model 1500 liquid scintillation counter. Counting efficiencies were determined by subsequently spiking one sample in 30 (or at least three in each sample set) with 15 to 30 mg of a known tritiated water sample and re-counting.

After completing the column elution, it was disassembled and the soil core was extruded, sectioning the sand at 1 cm increments. These soils were oven-dried, and subdivided and counted using the procedures outlined in section 4.3.5.

(c) In-Situ Soil Treatment Study

A schematic of the equipment arrangement for the in-situ soil decontamination test is given in Figure A.7. A 1 000 L polyethylene tank provided the leachant reservoir, and a calibrated sight tube provided measurements of the volume in the supply tank. Pump P-1, a variable speed large-volume Masterflex peristaltic pump, transferred the leachant to the in-situ test cell injection well. A float switch mounted in a short stilling well in the southeast corner of the test cell controlled the pump P-1, switching it on when the water level at the input end of the test cell fell to about 5 cm below surface and switching off when the water level reached grade. The pump P-1 was set at a speed to give about twice the flow rate established in the cell during the experiment. This ensured that the head at the injection end of the test cell would always remain near ground surface, but would avoid excessive head in the injection well and minimize upward flow immediately around the well.

Leachant solutions were prepared in batches. Water for the leaching solution was drawn from the CRL fire water supply system and delivered in a stainless steel tank by truck, daily or more frequently. The volume of water added to the supply tank, and the time of reading, were logged to provide a record of injection rates, and to determine the quantities of chemicals and tracer to be added. Intermediate readings of volumes and times were also periodically recorded.

During the addition of sodium dithionite, compressed nitrogen gas was injected through a diffuser at the bottom of the supply tank. After filling with water, a glove bag containing a bottle with a measured quantity of $Na_2S_2O_4$ was strapped over the tank hatch opening, and the tank was purged through a vent in the glove bag for 10 to 15 minutes with a nitrogen flow rate of about 30 $L \cdot min^{-1}$. The gas sweep rate was then reduced and maintained at 5 $L \cdot min^{-1}$ until the next batch of leachant was prepared. The powdered sodium dithionite was then added to the tank. During the acid addition of the test, pump P-2 (a Masterflex 7015 peristaltic pump) was used to transfer the appropriate volume of concentrated HCl into a calibrated 10 L translucent reservoir, which was then gravity-drained into the feed tank after it had been filled with water.

Pump P-3, a ⅓ hp glass-reinforced plastic centrifugal pump, was operated for 10 minutes after each batch of leachant was prepared to ensure complete mixing in the supply tank. System plumbing was stainless steel and polyethylene, using Swagelok connectors for the tube connections.

Pump P-4, another high-capacity variable-speed Masterflex peristaltic pump, was used to remove leachate from the downgradient end of the in-situ test cell, and to pump the leachate to a holding tank prior to its processing to concentrate the contaminants. The inlet for pump P-4 was placed in the withdrawal well at the depth where the water table at the withdrawal end of the test cell could be maintained at a desired level. Pump P-4 was run at a rate about 30% higher than the rate of leachate inflow to the withdrawal well, so that the water level in the well was held constant. A fraction collector (American Sigma) was also installed at the withdrawal end of the test cell, with its intake line placed deeper in the withdrawal well than the suction tube attached to pump P-4.

(d) Pilot-Scale Ex-Situ Soil Treatment

Ultrasonically-aided soil leaching was done in two ways: (1) using a rectangular Branson ultrasonic tank fitted with the laboratory-scale mixer to stir the slurry and prevent soil settling; (2) using a tubular Branson ultrasonic liquid processor. A 0.02 cm inside diameter (ID) stainless steel pipe was retroactively installed in the chamber of the ultrasonic liquid processor to protect the chamber's wall from the process liquid. Cooling water was circulated around the pipe for controlling process temperature and providing a medium for ultrasonic energy transfer. The total volume available to the process fluid in the pipe was 0.065 L (0.02 cm ID by 0.2 m). The circulation rate of the slurry was set between 10 and 15 L/min.

Chemical Pit Soil Leaching and Leachate Treatment

Equipment for the pilot-scale soil leaching experiments consisted of an ultrasonic tank, whereas the leachate treatment was performed with a tubular ultrasonic liquid processor (Figure A.8). The process water was heated in the 1,000 L polypropylene tank which was equipped with an overhead Lightnin mixer and two 5,000 W heaters. The water temperature in the tank was controlled by a temperature control system equipped with a type J thermocouple.

About 300 L of pre-heated water at the desired temperature was pumped to the 1,000 L filtration feed tank which was equipped with an overhead Lightnin mixer. Thirty kilograms of ground Chemical Pit soil was then added into the feed tank. The liquid-to-solid ratio for the soil leaching was kept at 10 to 1 due to the limitation of the transfer pumps. A pre-determined amount (4.2 kg) of concentrated hydrochloric acid was added to the tank to provide the desired acid concentration of 0.1 mol/L in the solution. The soil-leachant mixture was transferred to the ultrasonic tank system using a Sand Piper double diaphragm pump.

The slurry in the ultrasonic tank was circulated back to the feed tank by a double diaphragm pump. The solution pH and ORP (Oxidation-Reduction Potential) were monitored by means of a pH measurement system and an ORP measurement system. The sensors were calibrated using buffer and standard ORP solutions. The slurry was circulated continuously at a rate of 30 L/min through the ultrasonic tank until the desired process time (60 minutes) was reached. The process volume in the ultrasonic tank was kept at 15 L by adjusting the process pump rates.

Similarly, for soil decontamination and leachate treatment tests with the ultrasonic liquid processor (Figure A.9), about 30 kg of the ground contaminated soil and 300 L of process water were added to the filtration feed tank which was equipped with an overhead Lightnin mixer. The slurry was circulated through an ultrasonic liquid processor by a Sand Piper double diaphragm pump.

Concentrated hydrochloric acid was injected to the system via a check valve using a Milton Roy controlled volume pump. The pump was pre-set at a rate that gave the desired HCl concentration based on the process flow rate. Two levels of HCl concentration were used; they were: 0.05 and 0.1 mol/L. The acid injection point was located at upstream of and close to the ultrasonic liquid processor. The solution pH and ORP were measured by a bench-top pH/mV meter with proper electrodes.

Samples were taken from the sampling point located downstream of the ultrasonic equipment at desired time. The soil from the samples was immediately separated from the leachate to prevent further leaching using a pressure filtration unit with Whatman 541 filter paper (25 μm retention rating).

After the desired process time, the soil slurry was pumped from the feed tank to a frame-and-plate Perrin filter press for solid-liquid separation. The filter press had a cake capacity of 0.045 m^3 (1.6 ft^3) and a filter area of 4.14 m^2 (44.6 ft^2). The press consisted of 2 high density polypropylene head plates and 7 one-inch intermediate plates. The filter cloth was made of polypropylene with 3-5 cubic foot per minute (CFM) porosity. Before filtration, the filter cloths were pre-coated with Harborlite 800S filter-aid to improve the filtration performance.

The leachate from the filter press was stored in the conditioning tank (1,000 L polypropylene tank), and samples of leachate were collected for chemical analyses. The treated soil was washed by water until the solution pH was higher than 4. The soil was then air dried and removed from the filter press. Samples of the treated soil (without any filter-aid) were taken for chemical analysis. The rest of treated soil was drummed for disposal.

The leachate stored in the conditioning tank was circulated through an ultrasonic liquid processor using a Continental processing cavity pump. The ultrasonic liquid processor consisted of transducers and a cylindrical process chamber coupled to a generator. The transducers provided 30 kHz nominal ultrasonic frequency and were strategically arranged around the central process chamber so that energy was focused for maximum intensity. The dimensions of the processing chamber were 0.07-m diameter by 0.20-m long. However, a stainless-steel vessel with 0.3 L capacity was retroactively installed inside the chamber to protect the processing chamber surface from the high pH process liquid. Cooling water was continuously circulated around the stainless steel vessel to transfer ultrasonic energy and to control process temperature.

Calcium hydroxide (lime) was added to the conditioning tank to raise the solution pH to a desired level. The solution pH and ORP were monitored by a pH measurement system and an ORP measurement system. The sensors were calibrated following the standard procedures. The solution temperature was measured using a type J thermocouple. Sodium carbonate (20% excess) was added to the system for calcium precipitation after the desired solution pH was reached. The solution was circulated at a rate of 5.7 L/min through the ultrasonic liquid processor for a desired time, and then pumped to the internal feed tank of the cross-flow microfiltration unit. Samples were taken at different times downstream of the ultrasonic liquid processor and were filtered using a laboratory-scale filtration unit with 0.2 µm polypropylene microfilters. The filtrate samples were collected for chemical analysis.

The Memtech microfiltration unit utilizes cross-flow cartridges incorporating micro-porous hollow fibres to remove solids from the feed solution. The unit is equipped with four 0.2 µm polypropylene membrane modules which give a total of 4 m^2 filter area. The equipment comes with a patented backwash system to maintain the design processing rate. The backwash can be initiated manually or set by the built-in timer.

High pressure air is periodically forced from the centre of the fibres back across the membrane thereby expanding the fibre and allowing air to remove solids from the outside of the fibre. The solids are then removed from the modules by the action of the flush feed water. The microfiltration unit was usually operated at a process flow rate of 7.6 L/min (2 US gpm) during the tests. The filtrate from the unit was stored in the treated water tank, and the backwash solution containing 2 to 5 wt. % solids was stored in the backwash tank. The backwash solution was dewatered further using a tubular filter press.

The Exxpress tubular filter pressing consists of sequential cycles of loading the filter module followed by cake discharge. When feed liquid is introduced into the filter module under pressure, the liquid permeates through the tube wall and solids are retained inside of the tube. The loading cycle is completed when the solids layer reaches a predetermined thickness, and is controlled by a built-in timer. The cake discharge then commences by opening the module reject valve and traversing the module with squeeze rollers which removes the cake from the tube wall. The solids are transported out of the module by means of the flush liquid. The module is effectively cleaned during each cake discharge cycle by the rollers and by the action of the flush liquid. The filtrate from the filter press was temporarily stored in the filtrate tank and then pumped back to the conditioning tank for further treatment. The wet cake from the press was stored in a steel drum for secondary waste form study.

The treated water from the lime-soda treatment was pumped back to the conditioning tank for the second-stage treatment using powdered natural zeolite (TSM-140H clinoptilolite or ZS500H chabazite). The clinoptilolite (TSM-140H) was obtained from Steelhead Specialty Minerals, Washington, USA, and the chabazite (ZS500H) was supplied by Fisher Technical Development Inc., Columbia, USA. The procedure for the second-stage treatment was the same as the lime-soda treatment.

Fernald Soil Leaching and Leachate Treatment

The flowsheet for pilot-scale soil decontamination and leachate treatment tests for Fernald Incinerator Area soil is shown in Figure A.10. The configuration of the equipment was very similar to that for the Chemical Pit soil leaching using the ultrasonic liquid processor.

About 30 kg of the sieved contaminated soil and 300 L of process water were added to the filtration feed tank which was equipped with an overhead Lightnin mixer. Pre-heated water was used for the high temperature leaching tests. Leaching temperatures of 23 and 40 °C were used in the study. If applicable, an oxidizing agent ($KMnO_4$) was added directly to the feed tank.

The slurry was circulated through the same ultrasonic liquid processor used for the Chemical Pit soil leaching tests by a Sand Piper double diaphragm pump. The circulation rate of the slurry was set between 35 and 45 L/min.

A sample of the soil-water mixture was taken for reference from the sampling point located downstream of the ultrasonic liquid processor. The soil was separated from the water using a vacuum filtration unit equipped with a Whatman 3 filter paper.

Sulphuric acid was injected to the system as described under the Chemical Pit soil leaching treatment section using the ultrasonic liquid processor. Two concentrations of H_2SO_4, 0.1 and 0.25 mol/L, were used.

The slurry was circulated for a desired time (about 30 minutes) through the processor, and then pumped to a Perrin frame-and-plate filter press. The rest of the method is similar to the method described under the Chemical Pit soil leaching treatment system using the ultrasonic liquid processor. The leachate was stored in a 1,000 L polypropylene conditioning tank.

A pre-determined amount of iron, 10 g Fe^{+3}/L solution (as sulphate), was added to the conditioning tank to provide about 100 mg/L of Fe^{+3} in the leachate. The pH chemical (calcium hydroxide, sodium hydroxide or magnesium hydroxide) was added to the conditioning tank to raise the solution pH to a desired level. The solution pH and ORP were measured by a bench-top pH/mV meter with proper electrodes. A pre-determined volume (based on 1,500 mg H_2O_2/L) of 30% hydrogen peroxide solution was added.

The suspension of precipitate and solution was circulated at a rate of about 20 L/min through the ultrasonic liquid processor for a desired time, and then filtered using a Perrin frame-and-plate filter press. The filtrate was stored in the treated water tank, and the wet cake was drummed. Samples were taken during the test downstream of the ultrasonic liquid processor and were filtered using a vacuum filtration unit equipped with a Whatman 3 filter paper. The filtrate samples were collected for chemical analysis.

(e) Waste Form Evaluation

Solidification Agent

Portland cement was used to solidify the secondary waste generated from the Chalk river Chemical Pit soil leaching tests. Portland cement was chosen due to its: (1) low cost, (2) high shielding capability, (3) chemical stability (against damage and fire), and (4) water compatibility.

Cement has been widely used for the solidification/immobilization of hazardous, low-level radioactive and mixed wastes. Cement chemistry is complex because many different reactions occur depending on the composition of the cement mixture. The characteristics of most cements are due to the formation of hydrated calcium silicates, aluminates, or aluminate sulfates, or compounds of two or more of these groups.

The interactions of embedded waste species with cement chemistry can cause swelling, cracks, set time retardation, and weakening of the mechanical properties of the waste form if not formulated properly [Kasten et al., 1989]. The long-term durability of cement-based waste form is dependent on the chemistry of the waste, as well as the product waste form.

Soluble species are expected to leach from the cement matrix. A significant amount of calcium is usually leached from cement-based waste form. The leached calcium comes from soluble phases formed in the cured cement. The amount of strontium leached from cementitious material has been found to be directly proportional to the amount of calcium released from the cement matrix [Kasten et al., 1989].

Product Waste-Form Preparation

A waste (wet weight) to cement (dry weight) ratio of 1 to 1 was used to prepare the cemented waste. This ratio was selected based on the operation experience from a groundwater remediation facility at AECL's Chalk River Site. The secondary waste generated from the Chalk River soil leaching tests contained about 70% of water (wet cake from the filter press).

A known amount of the waste sludge was combined with per-determined amounts of cement and water. This mixture was stirred until it was homogeneous, and then poured into cylindrical moulds. A total of 12 samples were prepared with the same waste to cement ratio. The weights of the moulds and mixtures were measured. The cement-waste mixture was allowed to cure for at least 28 days. The solidified waste samples were then removed from the moulds, weighed, and prepared for the tests.

Dynamic Leach Test

The dynamic leach test used in this study is adapted from the American Nuclear Society Test ANSI/ANS 16.1-1986 [ANS, 1986]. The method differs from the American Nuclear Society method in that less leaching intervals are used and the overall test length is shorter (5 days instead of 90 days). The shorter leach time is recommended for cement-based waste form by USNRC [1991].

The ANSI/ANS 16.1-1986 procedure provides accumulation of data over a period of time to serve as a basis for indexing contaminants release from solid waste forms under controlled conditions. The procedure employs periodic leachant replacement to simulate the conditions of a continuous flow system. The leachant change-out occurs at the following intervals: 30 seconds rinse, 2, 7, 24, 48, 72, 96 and 120 hours. The leachant is controlled in a specified temperature range (17.5 to 27.5 °C), and the leachant volume to sample geometric surface area ratio is approximately 10 cm.

The dynamic leach test was carried out in 1,000 mL Pyrex beakers. The leachant was a known volume of distilled water (the leachant volume was approximately 10 times of geometric surface area of the specimen). The sample was suspended in the leachant with a piece of wire, wrapped several times around the sample and bent over the lip of the beakers. The specimen was first rinsed with a volume of water equivalent to the volume of the mould cavity. The sample was rinsed by immersion in distilled water of the same known volume as the leachant for 30 seconds. These two volumes of water were combined. The total volume content was then analyzed to determine the initial loss of contaminants from the specimen.

The rinsed sample was suspended in the leachant for an interval of 2 hours. At the end of this interval, the sample was removed from the leachate and placed into fresh leachant in a new beaker. The used beaker was rinsed, and the rinse was added to the leachate. This operation was repeated after 7, 24, 48, 72, 96 and 120 hours from the beginning of the test, with each leachate (with the beaker rinse water) being sampled, acidified and analyzed for the contaminants of interest.

Unconfined Compressive Strength

The compressive strength of the product waste samples was measured using Intron model 4206 mechanical tensile machine equipped with a computer for data collection. The recommended test procedure for compressive strength of cylindrical concrete specimens (ASTMC39) was followed closely. The maximum compressive strength was determined based on the load displacement and the sample's cross-sectional area.

4.3.4 Process System Monitoring

The operating conditions were categorized into: a) those which influenced the process directly and b) those which had minimal effects on process performance. Certain variables that influence the process to a smaller extent were maintained as fixed variables. The selection of the fixed variables was based on our previous experience.

In this project, the primary processing steps involved soil leaching and leachate treatments. The soil leaching was performed using either ex-situ or in-situ modes of operation, whereas the leachant treatment was carried out by ex-situ processing of the leachate using chemical precipitation and sorption. The leaching of soils was achieved with chemical leachants and soil-leachant suspension mixing using an ultrasonic field and/or mechanical agitation and flow field induced by pumping action. Specific leaching tests also included the addition of oxidizing or reducing chemicals, and sorbents. In certain instances, the leaching was also performed at elevated temperature. Similarly, the leachate treatment was performed using chemical precipitation and sorption techniques in the presence of an ultrasonic field and/or mechanical mixing involving pump induced flow mixing and mechanical agitation. The leachate treatment was conducted at room temperature. In soil leaching and leachate treatment experiments, the dewatering of the solid suspension was effected by pressure filtration involving cross-flow microfiltration and frame-and-plate filterpressing.

The key independent and dependent variables are summarized as follows.

Variables	Bench-Scale Tests	Column Tests	In-situ Field Test	Pilot-Scale Tests
(I) Soil Leaching				
(A) Dependent Variables				
- Untreated Soil Quality (M) and Index (D)	y	y	y	y
- Treated Soil Quality (M) and Index (D)	y	y	y	y
- Soil Particle Size (M)	y	y	y	y
- Leachate Composition (M)	y	y	y	y
- Contaminant Removal Efficiency (D)	y	y	y	y
- Treated Soil Wet and Dry Weight (M)	y	n/a	n/a	y
- Filtration Time (M)	n/a	n/a	n/a	y
- Leachate Recovery Rate (M)	n/a	y	y	n/a
(B) Independent Variables				
- Type of Contaminated Soil (V)	y	n/a	n/a	y
- Type of Leachant (V)	y	y	n/a	y
- Concentration of Leachant (V)	y	y	n/a	y
- Leaching Temperature (V)	y	y	n/a	y
- Leaching Time (V)	y	y	n/a	y
- Solution pH (V)	y	y	y	y
- Solution Eh (V)	y	y	y	y
- Mixing Power Input (V)	y	n/a	n/a	y
- Ultrasonic Frequency (V)	y	n/a	n/a	n/a
- Mechanical Agitator Speed (F)	y	n/a	n/a	n/a
- Liquid to Solid Ratio (F)	y	n/a	n/a	y
- Amounts of Oxidizing/Reducing Reagents Added (V)	y	y	n/a	y
- Filtration Pressure (F)	y	n/a	n/a	y
- Leachant Injection Rate (F)	y	y	y	y
- Leaching Process Rate (V)	n/a	y	y	y

Note: M: Measured; D: Determined; F: Fixed; V: Varied, y: parameter varied, measured or calculated and n/a: not applicable.

Variables	Bench-Scale Tests	Column Tests	In-situ Field Test	Pilot-Scale Tests
(II) Leachate Treatment				
(A) Dependent Variables				
- Leachate Composition (M) and Index (D)	y	n/a	n/a	y
- Treated Water Quality (M) and Index (D)	y	n/a	n/a	y
- Contaminant Removal Efficiency (D)	y	n/a	n/a	y
- Secondary Waste Wet and Dry Weight (M)	y	n/a	n/a	y
- Filtration Time (M)	n/a	n/a	n/a	y
(B) Independent Variables				
- Type of Leachate (V)	y	n/a	n/a	y
- Type of pH Modifier (V)	y	n/a	n/a	y
- Type and Concentration of Precipitant (V)	y	n/a	n/a	y
- Type and Conc. of Sorbent (V)	y	n/a	n/a	y
- Conditioning Temperature (F)	y	n/a	n/a	y
- Conditioning Time (V)	y	n/a	n/a	y
- Solution pH (V)	y	n/a	n/a	y
- Solution Eh (V)	y	n/a	n/a	y
- Mixing Power Input (V)	y	n/a	n/a	y
- Ultrasonic Frequency (V)	y	n/a	n/a	y
- Mechanical Agitator Speed (F)	y	n/a	n/a	y
- Amounts of Oxidizing/Reducing Reagents Added (V)	y	n/a	n/a	y
- Filtration Pressure (F)	y	n/a	n/a	y

Note: M: Measured; D: Determined; F: Fixed; V: Varied, y: parameter varied, measured or calculated and n/a: not applicable.

4.3.5 Sampling Analysis

(a) Bench-Scale and Pilot-Scale Ex-Situ Soil Leaching Study

Soil and solution samples were analyzed for several metals, radionuclides and Total Dissolved Solids (TDS). For the Fernald Incinerator Area soil, the samples were analyzed for: Al, Ca, Fe, Mn, Pb, U, SO_4 and TDS. For the Chalk River Chemical Pit Soil, the samples were analyzed for: ^{90}Sr, ^{60}Co, ^{106}Ru, ^{137}Cs, U, Ca, Fe and Total Dissolved Solids (TDS) [see Table B.7].

As detailed in the Project Test/QA Plan (Vijayan et al., 1994a, AECL Internal Document No. WMS-PP-56), the following methods were used for chemical and radiochemical analyses. Uranium in soil samples were measured by delayed neutron counting. Solution samples containing small amounts of uranium were analyzed using the laser fluorescence (Scintrex) method. Radionuclides in soil and solution samples were determined using beta scintillation counting and gamma spectrometry. Digested (with 10% HNO_3-microwave) soil samples and solution samples were analyzed for metals by Inductively Coupled Plasma Spectrometry. The sulphate in solution samples was analyzed by ion chromatography.

(b) Bench-Scale Soil Column Leaching Study

All of the soil samples were analyzed for ^{90}Sr by beta counting after mounting between 0.50 and 0.75 g of soil on stainless steel planchettes and measuring count rates using gas flow proportional counters fitted with guard detectors. Samples of CRL sands known to be free of contamination were used to determine backgrounds, and a series of planchette-mounted sands of various weights and spiked with known quantities of ^{90}Sr (traceable to a NIST reference ^{90}Sr solution) were used to define counter efficiencies. Soils spiked with ^{60}Co were also analyzed using the gas flow proportional counters to define counter efficiencies for this isotope.

A composite sample from ES-31 was analyzed by high-resolution gamma spectrometry. All other gamma analyses were performed with a Canberra-Packard 5530 automatic NaI gamma counter. Water and soil samples were counted in 20 mL vials, accompanied by blanks of a similar volume or mass, and standards prepared from a ^{60}Co stock solution traceable to NIST.

An aliquot of each water sample for ^{90}Sr analysis (20.0 mL) was pipetted into a standard polyethylene scintillation vial, and these were stored for at least 17 days (to allow for ingrowth of ^{90}Y) prior to Cerenkov beta analysis using a liquid scintillation counter (Canberra-Packard Model 1500). The same samples were also analyzed for ^{60}Co with the Model 5300 autogamma counter, and standard ^{60}Co solutions were analyzed for their Cerenkov efficiencies so that the ^{90}Sr+^{90}Y data could be corrected for the cobalt contribution.

(c) In-Situ Field Study

Soil cores recovered during drilling were logged on site for visual features and radiation survey measurements. The cores were sectioned at nominal 0.3 m increments, making adjustments to accommodate visible stratigraphic changes and core recovery. The soils were oven-dried, and all subsampling was done using mechanical sample splitters. Selected subsamples were analyzed for grain size distribution using standard ASTM procedures, to assist in stratigraphic correlation and for estimating hydraulic properties.

Water samples were collected from the multi-level piezometers by suction, attaching a peristaltic pump directly to the piezometer tube and pumping at least two tube volumes to waste before sample collection. Samples were stored in 20 mL polyethylene vials. The distribution of hydraulic head in the test cell was monitored through records of static levels in the multilevel piezometers made with an electric water level tape.

Samples of the test cell effluent were taken at 1-hour intervals and collected as 4-hour composites (i.e. four samples per bottle). After measurement of solution pH, the samples were filtered through 0.45 µm filters and acidified to a pH below 2. During the initial stage of the test, a separate Masterflex 7015 pump supplied a constant stream of water from the withdrawal well to a plexiglass flow cell containing a combination platinum electrode (Orion 90-01), connected to an Orion Model 407A meter and a strip chart recorder for redox potential measurement. The electrode was checked twice daily using Orion two-point test solutions. Methods for determination of the other chemical and radiometric parameters investigated in the field experiment were identical to those used in the bench-scale soil column leaching tests.

Prior to and during the in-situ soil decontamination experiment, measurements of downhole radiation fields were collected using a NaI detector housed in a waterproof probe, attached to a winch that allows for positioning to within 1 cm. The winch controller and the detector output were linked to a commercial portable multichannel analyzer or MCA (a Canberra Series 10), operated in multichannel scaling mode. Counts from the NaI detector (in this case, using a window that excluded only the lowest 1% of the spectrum) were accumulated in a single channel of the MCA until the winch moved the downhole probe some pre-set distance. Counts were then accumulated in the next MCA channel, building a record of activity versus depth in the hole being scanned. Data were downloaded to a PC for post-processing. Detector performance was monitored by counting a check source in a pre-defined geometry. Conversion from downhole count rates into radionuclide concentration was achieved by correlating pre-test borehole scan data with radionuclide concentrations measured on core samples.

The chemical and radiochemical methods used in the project and their detection limits are summarized in Table B.7 (Appendix B).

4.4 Quality Assurance

The primary goal of the project is to demonstrate the performance of soil and leachate treatment flowsheets to remove uranium and related metals, and radionuclides from actual contaminated soils using ultrasonically-aided chemical treatment. The waste influents include soils from Fernald Incinerator Area soil and Chalk River Chemical Pit soil, Ontario. The two year project involved laboratory-scale test in the first year (Phase 1) and pilot-scale studies (Phase 2) in the second year.

The detailed Test Plan/Quality Assurance Plan (TP-QAP) document was approved by USDOE/ METC on 1994 April 09. The TP-QAP document [Vijayan et. al., 1994a] describes in detail all aspects of the project including: 1) Project tasks, experimental design and procedure; 2) Management plan; and, 3) Quality assurance plan. The TP-QAP provides a detailed account of: experimental procedure control, procurement, equipment control, reagent control, sample control, analytical procedures, analytical QC checks, analytical quality objectives, data treatment, records, non-conformances, corrective actions, audits, QA review and QC reports to management.

In performing this project, all essential components of the TP-QAP goals described in our report [Vijayan et al, 1994a] have been met. The key QA/QC measures implemented are summarized as follows:

- All tasks and subtasks (actual numbering and planned tests) retained; for optimization tests, duplicate and other parametric tests were performed over and above the planned tests in the TP-QAP.

- All instrument calibrations, measurements, sampling and chemical/radiochemical analyses were followed as described in the TP-QAP.

- For every batch of waste influent tested, at least one sample per sub-batch was sampled and analyzed as required.

- Extensive efforts were made to maintain laboratory log books.

- The precision and spread in the lower limits of the chemical analysis results and their influence on contaminant removal calculations were accounted adequately by statistical calculations.

- Control of information flow and documentation including close supervision of technical staff on a day-to-day basis was maintained.

- All data, flowsheets and variables given in the text and in Appendices A and B were checked thoroughly by the personnel originating the data, and re-checked by a professional in the team and the Technical/Project Manager; all data were entered by LOTUS 1-2-3 spreadsheet and flowsheets were drawn using LOTUS FREELANCE Graphics software.

- Basic statistical calculations for establishing uncertainties based on 95% confidence limits were employed to ensure reliability of contaminant removal data.

- Chemical reagents used in the tests were obtained from the same source and the purity standards and lot numbers were monitored.

4.5 Data Treatment and Errors

4.5.1 Chemical Analysis

Errors reported with analysis results include both bias and precision components.

Bias was determined from the arithmetic mean of the percentage differences between a set of measured results and their accepted reference values. Precision was determined from the results of replicate experiments performed under identical conditions and incorporates error components due to sample preparation procedures as well as those associated with the instrument analysis. The precision corresponds to twice the standard deviation (2s), representing a 95% confidence level.

Analytical instrumentation was calibrated/checked prior to each batch of analysis. During the analysis of each sample batch, method performance tests, precision checks and bias checks were performed to ensure that the method was performing satisfactorily at the time the samples were analyzed and to obtain quantifiable parameters that can be used to verify the reliability of the analysis results [Vijayan et. al., 1994a].

4.5.2 Other Experimental Errors

Errors associated with other important variables, such as PCRE from soil or leachate can be caused by errors in the measurements of certain parameters. They include: solution pH, concentration of ion exchange and adsorbent materials, chemical conditioning time, solution mixing intensity, and feed flow rate to process equipment. Adequate controls of these variables are essential to minimize errors in the determination of the process target parameters.

Process measurement errors were evaluated by determining variance (s^2) in duplicate processing tests. This variance is an estimate of the overall error in the processing method. This overall error is the sum of errors from a number of sources. Thus

$$s_T^2 = s_A^2 + s_1^2 + s_2^2 + \dots\dots\dots$$

where S_A^2 is the error in chemical analysis, S_1^2, S_2^2, ... are errors in the control of various process parameters (e.g. solution pH, temperature, rate of reagent addition etc.). Each of these errors was not separately determined except the analysis error. We grouped all the other errors as experimental error (S_E^2) and determined its value from

$$S_E^2 = s_T^2 - s_A^2$$

S_T is determined from duplicate processing test results and S_A is known from replicate analysis. The experimental error is calculated from the above equation.

The calculated errors are given in Tables B.8 and B.9 as relative percent 2-sigma (2s%) values.

Important variables in the experiments (both bench and pilot-scale) include: temperature, ORP and pH of the solution, particle size and concentration of the adsorbent and other reagents, leaching and chemical conditioning time, slurry mixing intensity and slurry process flow rate, rate of reagent addition, and filtration time. Changes in these variables will affect the target parameters more or less depending on how critical they are in the processing. To minimize processing errors all variables were closely controlled during an experiment and in duplicate experiments. Measuring instruments (e.g., pH and ORP) were periodically recalibrated and cleaned and replaced, if necessary. Written experimental procedures were strictly followed.

Pilot-scale testing although involved complex experiments, the total error determined from duplicate test results indicated that the overall error was low as a result of tight control of experiments. The error was found to be large (PCRE for U was 14% (2s)) in bench-scale tests than in pilot-scale tests (PCRE for U was 4% (2s)). The large experimental error with the bench-scale results can be attributed to small amounts of feedstock used in the tests and their variability from one test to the other. Soil sample heterogeneity was a particular issue in establishing process performance with the pilot-scale tests involving short contact time reactions.

Sample Heterogeneity

(a) Fernald Soil

Uranium exists as very fine particles adsorbed on to the soil components. The distribution of uranium will depend on the adsorbability of the soil components, how the uranium dust was distributed on the area initially from incinerators, and how the water movement transported the uranium particles. Naturally, the uranium distribution will not be homogeneous in the soil.

We received two batches of well mixed Fernald Incinerator Area soil. In Batch 1 soil, we found that uranium was adsorbed more by clay and very fine sand fractions of the soil than by silt fractions. 84% by weight of the soil was fine silt and clay fractions (<38 μm) and 15% of the soil was fine sand and coarse silt (425 to 38 μm size). The soil was therefore classified as fine.

A 1 kg random subsample of Batch 1 soil was taken for uranium analysis. The subsample was put in a Roalox grinding jar with a few burundum balls and rolled on a roller for 30 minutes to break the lumps and homogenize the subsample. It was then placed on a polyethylene sheet, coned and quartered, and 5 test samples were taken for analysis. The analysis showed that it contained a mean uranium concentration of 527 mg/kg ± 11 % (2s%) relative error. The particle size distribution is shown in Figure A.12(a).

Another 1 kg subsample was ground for 16 hours with burundum cylinders (1 cm^3), and 5 test samples were taken. The particle size distribution is shown in Figure A.12(b). The figures show that grinding for 16 hours did not change the particle size distribution significantly. The analysis gave a mean uranium concentration of 559 mg/kg ± 9% (2s%). This indicates that grinding did not improve the homogeneity of the soil. All bench-scale leaching tests were done on this ground sample.

For pilot-scale tests, Batch 2 soil was used. A random sample was taken (1 kg), and gravel and pebble fractions were removed by wet screening over an 8 mesh screen. The -8 mesh (2.38 mm opening) slurry was filtered and the wet cake was dried. This dried cake was ground by hand with a mortar and pestle, mixed and test samples were taken for uranium analysis following the method described previously.

The analysis showed a mean uranium concentration of 548 mg/kg ± 28% (2s%). This indicates that the sample was not homogenized as well as the Batch 1 test samples.

For pilot-scale tests, soil from the Batch 2 drum was used. For each test, about 30 kg of grab sample was screened over an 8 mesh screen and the soil was transferred to a 1,000 L polypropylene feed tank. About 300 L of water was added to the feed tank and the resulting slurry was stirred. A slurry sample was taken, filtered and the wet cake was dried and hand-ground. The ground sample was then mixed well and two test samples were taken for analysis. These samples consistently showed about 4 to 9 % higher uranium value than that of the dry feed samples. This could be due to the absence of certain coarse particles in the slurry sample when the samples were being taken. Since fine particles adsorb uranium more than coarse particles, the uranium content is apparently higher by 10 %.

(ii) Chemical Pit Soil

The Chemical Pit soil had a particle size distribution of well-graded sand (Figure A.12(c)). Analysis of the soil showed a heterogeneous distribution of ^{90}Sr, ^{60}Co, ^{137}Cs and gross gamma. The mean concentrations with 2s% error were: ^{90}Sr: 1204 pCi/g ± 40%; ^{60}Co: 74 pCi/g ± 44%; ^{137}Cs: 1.72 pCi/g ± 88% and gross gamma: 75.7 pCi/g ± 44%. Therefore, the soil was ground to -200 mesh (-75 μm) for bench-scale tests. The analysis of the ground sample was: ^{90}Sr: 1370 pCi/g ± 25%; ^{60}Co: 77.4 pCi/g ± 52%; ^{137}Cs: 3.0 pCi/g ± 18% and gross gamma: 80.1 pCi/g ± 12%. Grinding decreased the inhomogeneity in all cases except for ^{60}Co, which showed an 8% increase in its 2s% value.

5.0 RESULTS AND DISCUSSION

5.1 Bench-scale Ex-situ Soil and Leachate Treatment

5.1.1 Soil Flotation

Several chelating agents were used as the "collector" in the soil flotation experiments.

Cupferron was selected based on the favourable results obtained in our earlier studies on the flotation of uranium ores [Muthuswami et al., 1983]. The Cyanex reagents are known for their selectivity to uranium in solvent extraction [Rickelton, 1993]. Ion Quest has been known for its effectiveness in the removal of uranium from oil media [Balint, 1993]. Tiron was selected based on its use as a leachant in the preliminary studies on Fernald soil leaching tests by Brainard and coworkers at Los Alamos National Laboratory [ORNL, 1993a]. Sodium silicate is generally used as a suppressant for silica and clay minerals in the mining industry. Bunker oil has been used to increase the hydrophobicity of the flotation agent, cupferron [Muthuswami et al., 1983].

(a) Preconcentration of Uranium in the Fernald Soil by the Flotation Technique

Twelve flotation tests were carried out on a bench-scale Denver flotation cell (Table B.10). In these tests five chelating agents (cupferron, ion quest, cyanex 302, cyanex 925 and tiron) under natural solution pH conditions with or without the addition of a reducing agent (sodium dithionite) were employed. In selected tests, a modifier (bunker C oil or sodium silicate) was added to improve floatability of the soil with respect to uranium.

Overall, the chelating agents used were not effective in selectively concentrating uranium. However, among the four chelating agents tested, the use of cupferron gave a concentrate ('float') that contained 40% of the mass floated and 55% (w/w) of the uranium present originally in the feed. The reason for this unsatisfactory result appears primarily due to the nature of the soil, which contains over 84% (w/w) fines (less than 38 μm particle diameter).

To verify this, we added sodium silicate as a depressant for gangue slimes and silicious gangue minerals [Fuerstenau, 1975]. By this procedure, the concentrate floated contained 72% of the uranium in the feed in 42 % of the mass. This shows that the uranium flotation is improved considerably, when the slimes are controlled.

To obtain a residue containing less than 35 pCi uranium/gram, it is necessary to float a minimum of 96% of uranium present in the original feed in 50% mass. Generally, for a viable application of flotation as a preconcentration technique, it is desirable to float 20 to 25% of the mass containing 90 to 95% of the targeted element [Muthuswami et al., 1983].

Calculated values for flotation yield (mass floated and uranium concentration) are summarized in Table B.11.

The results suggest that it may be possible to improve the effectiveness of cupferron to achieve the desired target by the addition of other modifiers and through optimization. However, this may need much closer examination of the process beyond the scope of the present study. Thus, we have not pursued flotation any further as a viable technique for the Fernald Incinerator Area soil.

(b) Preconcentration of Radionuclides in the Chemical Pit Soil by the Flotation Technique

The Chemical Pit soil consists mainly of sand and insignificant amounts of clay and silt materials. Since the radionuclide distribution was nearly uniform throughout the matrix, the use of flotation technique to preconcentrate the soil was not expected to be a viable scheme. However, selected flotation tests were performed using cupferron as a chelation collector with little success (Table B.11).

5.1.2 Soil Treatment by Ultrasonically-aided Chemical Leaching

(a) Fernald Incinerator Area Soil

Effect of Leachants

The effect of different leachants on contaminant removal are summarized in Figure A.13, and the most promising results are given in Tables B.12 and B.13.

Group I: Chelating Leachants (with and without Reducing/Oxidising Agents)

Leaching of the Fernald IA soil with only citric acid (pH=7.3) removed about 64% of the uranium. The addition of a reducing agent (sodium dithionite) decreased the uranium removal efficiency from 64% to 57% (for 0.3 mol/L citric acid), and from 64% to 53% (for 0.1 mol/L citric acid). The results show that leaching in a reducing environment is not favourable. Leaching under reducing conditions reduces Fe^{3+} to Fe^{2+} and as a result a majority of the iron in the soil is removed as a citrate complex in solution. Consequently, the availability of citrate ions for uranium dissolution is also reduced. In addition, the insoluble uranium(IV) compounds in the soil do not dissolve under reducing conditions. The overall effect is similar to that observed by Francis et al. [ORNL, 1993a]. Citric acid dissolved about 4 wt % of the soil.

The leachant, Ionquest 201 (a proprietary phosphonic acid reagent) was found to be effective for removing uranium in a single-stage leaching. At as low as 0.1 mol/L, ionquest gave a residual uranium concentration of about 110 mg/kg of treated soil. Increasing the leachant concentration to 0.3 mol/L had insignificant effect on the uranium removal efficiency. Similarly, the addition of a "synergistic" reagent AWA-1380 with ionquest 201 had no advantage in uranium removal from the Fernald IA soil.

The soil was leached in two stages, first with Sodium citrate-Sodium bicarbonate-sodium dithionite (CBD) at pH 7.3 and next with ammonium carbonate-bicarbonate-potassium permanganate at pH 7 after examining the most favourable results reported by Francis et al. [ORNL, 1993a] based on a three-stage process. Since their first-stage of the three stages was determined to be unnecessary, we employed only the last two-stages. Our first-stage leach reduced the uranium level from 559 mg U/kg to 185 mg U/kg and the second-stage leach reduced the uranium level further to 83 mg U/kg of treated soil. About 6 wt % of the soil was dissolved by CBD in the first stage and a further 3 % in the second stage.

Group II: Alkaline Leachants (with or without Oxidizing Agents)

Single-stage leach tests at 45 °C using a mixture of 0.3 mol/L Na_2CO_3 and 0.3 mol/L $NaHCO_3$ at a pH value of 9.3 produced a treated soil containing 171 mg U/kg, while 0.1 mol/L Na_2CO_3 and 0.1 mol/L $NaHCO_3$ yielded 225 mg U/kg of treated soil. In both cases only about 4 wt% of soil was dissolved in the leaching process.

In a two-stage leach, the first-stage was performed using a 2% solution of NaOCl at a pH value of 10.5. Following this, a second-stage leach with NH_4HCO_3 at a neutral pH value produced a treated soil with a TSQI of 5.1 at a mean temperature of 30 °C and a TSQI of 4.1 at 50 °C. At both leaching temperatures, the soil dissolution was about 6 wt.%. The slight improvement in the uranium removal is attributed to increased leach temperature. These values are similar to the values reported by Lahoda and Lin [Part 2, p. 2-7, in ORNL, 1993a]

A comparison of the uranium removal data between Na_2CO_3-$NaHCO_3$ and NaOCl-NH_4HCO_3 leach tests show that increasing the concentration of the leachant improves the uranium removal efficiency. There is no significant advantage in the use of sodium hypochlorite-ammonium bicarbonate over sodium carbonate/bicarbonate mixture.

Group III: Acid Leachants (with or without Reducing and Oxidizing Reagents)

Hydrochloric acid leaching at 0.1 mol/L (final pH = 1.5) produced TSQI values of 5.1 in stage 1 and 2.5 in stage 2 leaches; 0.5 mol/L HCl (final pH =) gave TSQI values of 2.0 (stage 1) and 1.5 in stage 2 leach. However, 0.1 mol/l HCl with 2% NaOCl as the oxidising agent, having a final pH value of 5, gave TSQI values of 10.6 (stage 1) and 10.7 (stage 2). Similarly, a leachant consisting of 0.5 mol/L HCl and 2% NaOCl, with a final pH of 3.3, gave TSQI values of 10.3 and 10.6 in leach stages 1 and 2, respectively.

As expected at these final pH values, uranium is precipitated as hydroxide and as a result is not leached into solution completely. This illustrates a need for a uranium complexing agent or low pH to keep uranium in solution.

A single-stage leach using a leachant consisting of 0.005 mol/L HCl and 0.01 mol/L $FeCl_3$ gave a TSQI value of 9.3. When the concentration of the leachant was increased by ten fold, a TSQI value of 3.5 was obtained. These results showed that the use of higher acid strength together with an oxidant appear to improve the removal of uranium from the Fernald soil.

Soil leaching with 0.1 mol/L H_2SO_4 in the presence of an oxidising agent (air, $KMnO_4$ and $Fe_2(SO_4)_3$) produced TSQI values in the range of 1.2 to 2.3. The low TSQI value corresponds to usually a two-stage leach, while the high TSQI value corresponds to a single-stage leach.

The use of a leachant consisting of 0.3 mol/L H_2SO_4 and an oxidising agent gave TSQI values in the range of 1.1 to 1.9 in a single-stage leaching.

Soil leaching with a 0.5 mol/L H_2SO_4 when used in the presence of an oxidising agent gave TSQI values of 1.3 in stage 1 leach and 0.6 in stage 2. Results from several two-stage leach tests, where the first stage leach was performed using 0.5 mol/L H_2SO_4 and a reducing agent ($Na_2S_2O_4$) followed by a second-stage oxidative acid leach, showed that the first-stage leach reduced a FSQI value of 10.6 to a TSQI value in the range of 2.1-4.1 and the second-stage oxidative leach gave TSQI values in the range of 1.1 to 1.5.

The results suggest that the first-stage reductive leaching step does not contribute to the overall uranium removal efficiency, and a single-stage oxidative leach is, therefore, sufficient.

Effects of Solution Redox Potential and pH

In general, uranium removal was best achieved when leaching was performed in an oxidising environment, reflected by the final solution emf values in excess of 600 mV (Figure A.14). However, the solution pH is equally important on the overall leaching effectiveness, especially for non-complexing leachants such as HCl. Overall, in the case of mineral acid leachants (Group III leachants), in addition to relatively high solution emf values, low solution pH values (less than 1) were found to be necessary to reduce uranium concentration in the treated soil to the target level.

For near-neutral soil leaching involving alkaline leachants (Group II leachants), high solution emf value and high concentration of carbonate ion are required for high uranium removal. This is because there exist competing equilibria between uranyl hydroxide precipitation and uranyl carbonate complexing and dissolution.

Effect of Mixing Energy Input on Uranium Removal

The effects of mechanical and ultrasonic energy inputs on uranium removal from Fernald soil are illustrated in Figure A.15 The results suggest that increasing ultrasonic energy input has no advantage in improving uranium removal. This behaviour can be explained in terms of a "negative cavitational" effect.

Mechanically-aided mixing on uranium removal appears to be a reversal of the ultrasonic effect - the higher the energy input, the higher the amount of uranium removed from the soil. Since mechanical mixing does not produce cavitational effects, an increase in the uranium removal is expected to be caused by an increase in the energy input for kinetically controlled processes such as uranium oxide dissolution in Fernald soil leaching.

The results show that (Figure A.15 low ultrasonic input energy (as low as 15-20 kJ/L) is sufficient to remove uranium from Fernald soil. Increasing input energy further has no beneficial effect on uranium removal.

Figure A.16 shows the relationship between power, time and number of leach-stages on uranium removal. At two power input values (85 and 300 W), the leaching time was varied to achieve different energy inputs. The results demonstrate that increasing the ultrasonic power input from 85 W to 300 W (an increase of ~250 %) resulted in an increase in the uranium removal efficiency or reduction in the uranium concentration in the treated soil from 79.8 ± 6.4 to 73.3 ± 3.6 mg/kg for single-stage leaching, and from 44.9 ± 5.3 to 37.8 ± 3.4 mg/kg for two-stage leaching. This corresponds to a reduction in uranium concentration of 8 % for single-stage and 16 % for two-stage leaching. This suggests that there is no significant advantage in performing soil leaching at high ultrasonic energy. The use of low ultrasonic energy coupled with fluid circulation mixing (pump) appears to provide optimum uranium removal performance.

Effect of Leaching Temperature

At low leachant concentrations, increasing the leaching temperature has a beneficial effect of lowering further the uranium level in the treated soil. For the range of temperatures examined (23 to 75 °C), it appears that increasing the temperature leads to a lowering of the uranium level in the treated soil by about 0.5 mg U/kg to 1.5 mg U/kg. However, when sulphuric acid concentration was increased to 0.5 mol/L, the temperature effect was not evident after taking into consideration experimental and analysis errors.

Soil Dissolved During Leaching

In single-stage leaching, acid leachants dissolved about 5 to 10 wt% (depending on the acid concentration) of the soil, while with alkaline leachants, about 4 wt% of the soil was dissolved. Buffered chelating leachants dissolved soil in the range of 4 to 8 wt%, depending on the type and concentration of the chelating agent. The overall amount of soil dissolved in the combined two-stage acid leaching trials was found to be in the range of 10 to 15 wt%.

(b) Chalk River Chemical Pit Soil

Effect of Leachant

The effect of leachants on the removal of ^{90}Sr and gamma emitters (^{60}Co and ^{137}Cs) in soil leaching through ultrasonic mixing is summarized in Figure A.17. The measured and calculated results for the most promising leachant are presented in Table B.14. The ultrasonically-aided leaching time for the tests was generally kept at 3 minutes.

Group I: Chelating Leachants (with and without Reducing/Oxidising Agents)

Chemical Pit soil leaching with only citric acid (pH = 7.3, Eh = 160 mV) removed about 70% ^{90}Sr and 40% gross gamma emitters (^{60}Co and ^{137}Cs).

At a concentration of 0.3 mol/L, Ionquest 201 (a proprietary phosphonic acid reagent) removed about 78% ^{90}Sr and 63% gross gamma in single-stage leaching. At 0.1 mol/L concentration, ionquest showed a similar removal efficiency. The solution pH and Eh values were similar for these leaching tests at 1.6 and 360 mV, respectively.

With the addition of a synergistic reagent, AWA-1380, to a 0.3 mol/L Ionquest 201 solution, the ^{90}Sr removal efficiency was increased to 94%, while removal efficiency for gamma emitters was 17%. The solution pH for this test remained at 1.6, but the solution Eh was very low (-38 mV).

Single-stage leaching with Sodium citrate-Sodium bicarbonate-sodium dithionite (CBD) at pH 7 was found to remove about 84% ^{90}Sr and 53% gamma emitters at a solution pH of 6.8 and an Eh value of -700 mV. The CBD leaching was performed because it has been well-known that citrate ion has the ability to complex with a number of metal ions including Cs^+, Sr^{2+}, Fe^{2+}, Co^{2+} and Fe^{3+}. Among the metals of interest, Cs^+ has the lowest complex formation constant and Fe^{3+} has the highest formation constant. A second-stage leaching of the residue from the CBD leach with ammonium carbonate-bicarbonate-$KMnO_4$ solution did not show further improvement to soil decontamination.

The above soil decontamination results using selected chelating agents show that the contaminant removal efficiency, although reasonably high, does not meet the target value of 35 pCi/g for the treated soil.

Group II: Alkaline Leachants (with or without Oxidizing Agents)

Single-stage leach tests at 50 °C using 0.3 mol/L Na_2CO_3 and 0.3 mol/L $NaHCO_3$ at a pH value of 9.7 removed about 50% ^{90}Sr and 40% total gamma, whereas the 0.1 mol/L leach gave a removal efficiency of about 40% and 30% for ^{90}Sr and total gamma, respectively.

It should be noted that the carbonate compounds of all metals with the exception of Group I metals are insoluble in water and as a result the relatively low removal efficiencies obtained for the dominant ^{90}Sr and ^{60}Co in the Chemical Pit soil can be justified.

In a two-stage leach test, the first-stage was performed using a 2 % solution of NaOCl at an average pH value of 10.5. Following this, a second-stage leach with NH_4HCO_3 at neutral pH removed about 83% ^{90}Sr and 26% total gamma at 50 °C and 67% ^{90}Sr and 53% total gamma at 60 °C. At both leaching temperatures, the soil dissolution was in the range of 1.1 to 1.4 wt.%.

The relatively high contaminant removal efficiency (over carbonate leach) is evidently due to the high solubility of bicarbonate compounds of ^{90}Sr in water. The lower extraction of ^{90}Sr at higher temperature (60 °C) is due to the decomposition of HCO_3^- to CO_2 and CO_3^{2-} and consequent precipitation of ^{90}Sr.

Our results for residual contaminant concentration in the treated soil (using NaOCl-NH_4HCO_3 based on ultrasonically-aided leaching for a period of 3 minutes) are 242 pCi ^{90}Sr/g and 60 pCi total gamma/g at 50 °C, and 462 pCi ^{90}Sr/g and 38 pCi total gamma/g at 60 °C, starting from an average feed concentration of 1204 pCi ^{90}Sr/g and 75.7 pCi total gamma/g.

Group III Acid Leachants (with or without Reducing and Oxidizing Reagents)

Soil leaching at 50 °C with 0.01 mol/L HCl combined with 0.01 mol/L $FeCl_3$ at a solution emf of 700 mV removed of 75% of ^{90}Sr and 45% of total gamma. Leaching with 0.1 mol/L HCl (pH = 1) or with 0.5 mol/L HCl (pH = 0.4) with a solution Eh of 550 mV, with no oxidising agent present, removed about 90% ^{90}Sr and 70% total gamma. However, leaching with 0.1 mol/L HCl with a reducing agent (sodium dithionite) gave 97% removal for ^{90}Sr and about 74 to 92% for total gamma. The solution Eh was -40 mV. The results show a slight advantage in the HCl leach with the addition of a reducing agent.

Chemical Pit soil leaching results with different concentrations of HCl (with and without the addition of a reducing agent) suggest that the use of 0.1 mol/L HCl with dithionite in two stages can meet the 35 pCi/g target based on the total activity (^{90}Sr + ^{60}Co and ^{137}Cs).

Chemical Pit soil ground to -200 mesh size (-75 μm) when leached in a single-stage with 0.1 mol/L HNO_3 (emf = 400 to 474 mV) with the addition of small amounts of NaF gave in excess of 97% removal for ^{90}Sr and 82% for total gamma. The unground sample, however, showed lower removal for ^{90}Sr (90%) and total gamma (64%). A two-stage leaching of the ground soil with 0.1 mol/L HNO_3 alone gave removal efficiencies of 94% for ^{90}Sr and 76% for total gamma.

Although HNO_3 acid leach results show promise, the TSQI value is 1.5 to 3 times the target 35 pCi/g for total radioactivity in the treated soil.

Leaching of unground soil feed with 0.1 mol/L and 0.3 mol/L sulphuric acid gave poor values for residual activity in the treated soil, typically 10 to 12 times the target 35 pCi/g. However, the use of 0.1 mol/L H_2SO_4 for leaching the ground soil in two leach stages gave a total activity in the treated soil which was 4 times the target activity. Addition of a reducing agent with 0.1 mol/L H_2SO_4 in the two-stage leaching did not improve the treated soil quality. Poor leaching may be due to the low solubility of $SrSO_4$. Among the acid leachants tested, a solution of 0.1 mol/L HCl combined with a reducing agent such as $Na_2S_2O_4$ gives the most promising residual concentration values for ^{90}Sr and total gamma.

The order of soil leaching performance may be summarized as:

HCl + Reducing Agent > HCl > HNO_3+NaF > HNO_3 > H_2SO_4 or H_2SO_4 + $Na_2S_2O_4$

Effect of Solution Redox Potential and pH

Bench-scale soil leaching results for ^{90}Sr and total gamma removal show (Figure A.18) that soil decontamination was effective when the solution Eh was less than 400 mV and the pH value was in the range of 0.5 to 1.2.

Effect of Mixing-Energy Input on Contaminant Removal

Previous studies [for example, Mason, 1990] on chemical reactivity enhancements through the application of ultrasonic mixing suggest that increasing the energy input beyond a "threshold energy level" has no beneficial effect, which has been attributed to "negative" cavitational effects (see section 3.0).

In the present study, ultrasonic energy input of 30 to 100 kJ/L was used. However, the majority of experiments were done at a relatively high energy inputs. At the low-end of energy inputs, lowest values for residual uranium concentration in the Fernald soil were measured (Figure A.15). However, this trend was altered slightly (Figure A.19) for the case of ^{90}Sr removal from Chemical Pit soil - an increase in the ultrasonic energy decreased slightly the removal efficiency of ^{90}Sr, whereas the removal of gamma emitters remained essentially constant (within the experimental and analysis errors).

Generally, ultrasonic cavitation is reduced when the system temperature is increased, especially to near the solution boiling point [Mason, 1990]. In contrast, cavitation is essentially absent in mechanical mixing. Increasing the temperature of mechanically-agitated leaching of Chemical Pit soil increased the removal efficiency for ^{90}Sr. A significant reduction in ^{90}Sr removal occurred for ultrasonically-aided leaching when the energy input was increased.

The above effect was not observed for total gamma removal because: a) the initial amount of gamma present in the soil was low (only about 5% of the ^{90}Sr value); and b) 2s% values for gamma analysis were high in the range of 10 to 20%, which would have masked possible variations in the removal data.

Effect of Leaching Temperature

The effect of leaching temperature on ^{90}Sr removal was not appreciable (Table B.14), whereas increasing the temperature showed an increase in the removal of total gamma activity. The reason for the observed effect is not evident from the present experience and extent of variable interactions.

Soil Dissolution During Leaching

On average, the acid leachants dissolved 1 to 6 wt% of the soil in single-stage leaching (depending on the concentration of acid) and about 10 wt% in two-stage leaching. The alkaline and chelating leachants dissolved only about 1 wt% of the soil.

5.1.3 Soil Leachate Treatment

(a) Fernald Soil-Leachate Treatment

The feed assay for leachate composites obtained from soil leaching with H_2SO_4 is given in Table B.15. The leachate-treatment results at room temperature using ultrasonic and mechanical mixing are given in Table B.16 (for uranium removal) and in Table B.17 (for removal of other metals).

i) Effect of Precipitating Agents and Sorbents on Uranium Removal

The addition of lime alone to leachate from H_2SO_4 soil leaching at a solution pH of 4 removed only about 24.5% uranium (Figure A.20). The removal is accomplished primarily through uranium sorption by $CaSO_4$ precipitate. When the pH value was raised to 10 with lime, with the simultaneous addition of Fe^{3+} floc and H_2O_2, the overall uranium removal was increased to 97.7% in two stages. This removal corresponds to a treated leachate quality index of 1.8 (110 μg/L), with reference to US drinking water guidelines (see below).

It is interesting to note that the addition of limestone ($CaCO_3$) with H_2O_2 and Fe^{3+} floc at a low solution pH value (e.g., pH = 6) reduced uranium from an average concentration of 42 mg U/L to 0.5-1.7 mg/L. The drinking water guideline for uranium is 60 μg/L [USEPA, 1990] and 290 μg/L [ICRP, 1977].

Leachates from HCl and CBD soil leaching when subjected to similar precipitation-sorption treatment (as leachate from H_2SO_4 soil leaching), gave poor uranium removal results (Figure A.21), suggesting a need for a different treatment approach. The treatment of carbonate/ bicarbonate leachate was not performed. It is anticipated that a two-stage process based on acidification with H_2SO_4, followed by uranium precipitation at alkaline conditions using magnesium hydroxide and H_2O_2 will be required.

ii) Removal of Total Dissolved Solids (TDS)

A summary of TDS removal results is shown in Figure A.21. For the precipitation-sorption treatment, leachate from H_2SO_4 soil leaching provided a TDS value of about 3,500 mg/L in the treated water. The TDS values in the treated water for leachates from HCl and CBD soil leaching were very high in the range of 20,000 mg/L (for the HCl leachate system) and in excess of 100,000 mg/L (for the CBD leachate system).

To meet the USEPA drinking water guideline for TDS (500 mg/L), the treated water must be processed further in a polishing system utilizing process technology such as nanofiltration. However, for discharges in sewers, sanitary drain, and combined sewer-sanitary discharge systems, additional treatment may not be necessary to meet industrial discharge guidelines.

iii) Effect of Ultrasonic Energy Input on Uranium Removal

The results summarized in Figure A.23 suggest that lower ultrasonic-energy inputs are generally favourable for uranium removal from soil leachates. For the lime-H_2O_2-Fe^{3+} system, energy input of about 30 kJ/L appears to be adequate.

(b) Chemical Pit Soil Leachate Treatment

i) Effect of Precipitating Agents and Sorbents on Contaminant Removal

Three groups of treatment schemes using a combined precipitation-sorption method in the presence of a fixed 20 kHz ultrasonic field were employed to remove the radionuclides and other metals present in the soil leachate produced from Chemical Pit soil leaching tests. The treatment schemes included: 1) lime-soda addition (Serial #66, 68-72); 2) lime-soda-powdered natural zeolite addition (Serial #73-78); and 3) lime-soda-zeolite with an additional stage of either zeolite addition (Serial #79) or addition of copper sulphate + potassium ferrocyanide (Serial #80).

Composite samples of soil leachate, obtained primarily from soil leaching tests using HCl, were used as feed (see feed assay in Table B.18) for the leachate-treatment tests. The results for leachate treatment and the process conditions employed are given in Table B.19.

As ^{90}Sr is the dominant contaminant in the soil leachate, the basic treatment approach was to co-precipitate Sr as $SrCO_3$ along with $CaCO_3$ by the addition of lime and soda at an alkaline pH before adding zeolite to scavenge ^{90}Sr by ion exchange. This technique, as shown in a previous study [Vijayan et al., 1994; Buckley et al., 1992], removes calcium ions and strontium ions simultaneously. Otherwise, calcium ions reduce the effectiveness of ^{90}Sr removal by ion-exchange with zeolite because of ionic competition. Since a nearly total removal of ^{90}Sr is desired to meet the drinking water guidelines [USEPA, 1990; ICRP, 1977], a combined precipitation and ion-exchange method is required.

Contaminant-removal results (Figure A.22) demonstrated that leachate treatment using lime, soda and powdered zeolite can readily meet the ICRP guideline for maximum allowable concentration for ^{90}Sr, ^{60}Co and U. The uranium removal data demonstrated the process met the USEPA drinking water guideline.

The ^{137}Cs activity in the leachate was generally below the sample detection limit.

Because the Sample Detection Limit (SDL) in the small sample volume used for radiochemical analysis was too high, it was not possible to verify the effectiveness of ^{90}Sr removal with the USEPA drinking water guideline. Also, as the USEPA [1990] guideline was not available for ^{60}Co, an earlier guideline [US FED REG, 1986] was used instead.

Data for the removal of ^{90}Sr and ^{60}Co show that the leachate treatment, using lime + soda + zeolite powder in the presence of an ultrasonic field, is sufficient to meet the drinking water guideline(s).

ii) Removal of Total Dissolved Solids (TDS)

The TDS value for the treated leachate from HCl soil leaching was of the order of 21,000 mg/L, whereas that of the H_2SO_4 leachate was about 8,000 mg/L. The relatively high TDS was also due to the presence of sodium ions from Na_2CO_3 addition in the precipitation step. In this context, the use of controlled addition of CO_2, instead of Na_2CO_3, would be beneficial to reduce the TDS significantly, thereby reducing the load on the downstream polishing system for final treatment prior to discharge.

iii) Effect of Ultrasonic Energy Input on Contaminant Removal

The results for ^{90}Sr removal from the soil leachate show (Figure A.24) that increasing the ultrasonic energy for ^{90}Sr removal through precipitation with lime-soda, and precipitation-ion exchange with lime-soda-powdered zeolite did not improve the removal efficiency.

In summary, on the basis of the bench-scale test results using Fernald Incinerator Area and Chalk River Chemical Pit soils, an integrated ex-situ soil decontamination and soil-leachate treatment flowsheet was designed. A schematic of the flowsheet is given in Figure A.42 and preliminary process parameters are given in Table B.20.

5.2 Bench-scale Soil Column Leaching Study

Bench-scale soil column leaching results using columns B, D and C, respectively, are given in Figures A.25 to A.27. The column properties and test conditions together with the calculated porosity and dispersivities are summarized in Table B.21. The porosity and dispersivity values were determined from tritium-tracer elution curves and fitting the data with a 1-dimensional model. Column B was found to have a longitudinal dispersivity of 0.06 cm, while fits to the Columns C and D data provided dispersivities twice as large (0.14 cm). All of these dispersivities were low, suggesting acceptable homogeneity in the columns.

While the columns were being packed with the composite sand from ES-31, three samples were taken and analyzed to provide the initial inventory of ^{90}Sr and ^{60}Co in the columns. Through an error, those samples were analyzed along with the post-leaching column fractions, after the column elutions had been completed. Results for ^{90}Sr ranged from 7.9 to 13.1 Bq/g, and it had to be assumed that the heterogeneities in the ES-31 composite sand responsible for these variations were also present in the column packings. Subsequent re-homogenization of the bulk sample and analyses of 5 sub-samples provided average ^{90}Sr and ^{60}Co concentrations of 8.01(±2.04 at 1σ) and 0.54 (±0.07 at 1σ) Bq/g, respectively. These concentrations have been used in the column inventory calculations, but it must be recognized here that the actual ^{90}Sr inventory in each column may be as much as 25% different than the mean, and that significant heterogeneities in contaminant loadings may have existed in the columns.

Column B was used to test the most successful leaching agent (sodium dithionite followed by HCl) identified in the bench-scale ex-situ leaching tests (Section 5.1.2(b)). Sodium dithionite at a concentration of 770 mg/L was injected for the first 2.5 pore volumes of leachant added to the column; at this point, the column effluent Eh had fallen to that of the dithionite feed (-540 mV). The column feed was then switched to 0.1 mol/L HCl for the remainder of the test. Figure A.25 shows the solution Eh, pH, and concentrations of ^{90}Sr and Fe in the column effluent versus pore volumes eluted following the start of leachant addition. Both ^{90}Sr and iron show a peak in release concentrations that occurred as the column oxidation capacity was exhausted and the effluent Eh fell rapidly to below -400 mV. Iron concentrations in these effluents reached 750 mg/L, a factor of 6 higher than iron concentrations observed with any of the acid leachants. Peak ^{90}Sr concentration was much higher than that for leaching without the presence of sodium dithionite (Figures A.26 and A.27). The fall in effluent Eh to values below -500 mV was accompanied by a decrease in effluent pH to between 3.5 and 4.5. It appears that at this point in excess of 90% of ^{90}Sr had been already removed. The subsequent arrival of the 0.1 mol/L HCl front rapidly drove the column effluent pH down to 1.2, similar to that of the feed. Integration of the ^{90}Sr concentrations measured in the column effluent yields a removal of 117% of the calculated initial inventory in the column. This high removal might be due to experimental and analytical errors for the column effluent. Post-leaching sand analyses provide a radiostrontium removal of 89%. There was much better agreement between the effluent and soil-based removals calculated for ^{60}Co (63 and 62%, respectively).

Column C was treated with 0.1 mol/L HCl at a temperature of 5 °C, while Column D used the same leachant at room temperature (25 °C). This pair of tests were conducted in part to provide some gauge for comparing results from the bench-scale leaching tests (conducted at room temperature or above) with that at in-situ temperatures. Figures A.26 and A.27 display solution pH, ^{90}Sr, and Fe concentrations in the column effluents, and removal efficiencies are listed in Table B.21. In both cases, between 83 and 90% removals of ^{90}Sr were determined from the effluent and post-leaching soil data. Calculated percentage removals of ^{60}Co were more variable, ranging from 40 to 92%. The most obvious difference between the two tests was the greater intensity of iron leaching at the room temperature (Column D), where "steady-state" iron concentrations were a factor of three higher than those in the low temperature test (Column C). In addition, the peak in ^{90}Sr release from the room temperature test is slightly earlier and broader than that observed from the low temperature test. This implies that the leaching kinetic is faster at higher temperature.

5.3 In-situ Soil Treatment Field Study

5.3.1 Test Cell Initial Conditions and Hydraulic Properties

To delineate the distribution of materials and contamination in the test cell, soil coring was conducted at the locations for the injection and withdrawal wells, and for the Bin-2, 4, and 6 monitors (Figure A.6). The other monitoring locations were washbored only. The soil coring and monitor installations for all but the Bin-8 and 9 monitors was done before the test cell was driven into the aquifer.

A stratigraphic section through the test cell, based on the logs from the five cored boreholes and augmented with 14 grain size analyses covering most of the samples from the injection and withdrawal wells, is shown in Figure A.5. Although some of the organic soils were removed from the test area during site preparation, an irregular layer about 0.15-m thick covered the surface of the test cell. Because of the drawdown required over most of the test cell area during the leaching test, it was anticipated that the organic soils would be a minimal component of the experiment, and this was subsequently found to be the case. As a result, only limited characterization of the organic soils was performed.

Fine sands represent the bulk of the material in the test cell. Twelve samples of this sand were sieved - the overall mean grain size was 0.18 mm, with individual sample means ranging from 0.16 to 0.19 mm. The range of grain sizes in the fine sand is very limited, and using Folk and Ward's inclusive graphic standard deviation (0.46 to 0.601 ϕ) places all sands in the well sorted category. No direct determinations of porosity were made for any of the test cell samples, but from previous measurements in the area [Parsons 1960] a value of 0.40 was assumed.

Hydraulic conductivity for the fine sand was estimated using the Hazen and Masch & Denny grain size correlation procedures. The Hazen estimate averages 1.1×10^{-4} m/s, while the average Masch & Denny estimate is 7.7×10^{-5} m/s.

Two horizons in the test cell (one was around an elevation of 164.7 m and one was present at the base of the fine sands at the north end of the test cell) are more highly oxidized than the bulk of the fine sands (see Figure A.5). From these data, one cannot determine whether the oxidized horizons reflect variations in hydraulic conductivity or if they are the result of variable aqueous chemistry in the aquifer.

Throughout the test area the fine sands were underlain by a stratum of medium-fine sands, generally less than 0.5 m thick and in all cases located immediately above the clayey silt stratum. Samples of the medium-fine sand from the injection and withdrawal well boreholes were analyzed for grain size distribution. The mean grain size provided by these tests was 0.22 mm, with an inclusive graphic standard deviation of 0.56.

Because of the coarser mean grain size, and the similar degree of sorting, both the Hazen and Masch & Denny estimation procedures indicate hydraulic conductivities of 1.8×10^{-4} and 1.4×10^{-4} m/s, respectively, almost a factor of two greater than those for the fine sand. Apart from this, and an absence of more highly oxidized zones in the gary-brown medium-fine sands, properties of this unit appear no different than those of the overlying fine sands.

The clayey silt stratum beneath the medium-fine sands represents the lower boundary of the portion of the flow system that is of interest here. There was no evidence for Chemical Pit contaminants in the underlying till. Analysis for grain size distributions in the clayey silt was not made. However, estimates made previously for clayey silt samples in the vicinity of the test area suggested that the clayey silt contained up to 43 % of clay-sized particles and hydraulic conductivity values in the range of 1.8×10^{-6} to 6.5×10^{-8} m/s. By comparison with hydraulic conductivity values for sands, the clayey silt stratum can be treated as an impermeable lower boundary in the test cell.

5.3.2 Initial Radionuclide Inventories

The radiochemical methods used in the field analysis for ^{90}Sr and ^{60}Co are described in section 4.3.5 and their detection limits are summarized in Table B.7 (Appendix B).

Only the dominant isotopes (^{90}Sr and ^{60}Co) were analyzed in the field test. The analytical methods used for sample analysis are described in section 4.3.4. Figures A.28 and A.29 display the distribution of ^{90}Sr and ^{60}Co along the longitudinal centerline of the test cell. The contour plots were produced using Golden Software's Surfer package, with linear kriging of concentrations measured at the points marked on the sections, and a 2:1 horizontal to vertical anisotropy in point selection for interpolation. Pre-test inventories calculated from the gridded data were 136 MBq (3.68 kCi) of ^{90}Sr and 3.8 MBq (0.10 kCi) of ^{60}Co; with a total mass of contaminated sand in the test cell of 13.92 metric tons, the average soil concentrations are 9.8 and 0.27 Bq/g for ^{90}Sr and ^{60}Co, respectively.

Gamma scanning of the 3.2 cm inside diameter PVC pipes was started at the beginning of the experiment, and were repeated at intervals of between 12 hours and 4 days, depending on the location of the leaching front in the test cell. The gamma scanning data showed a large peak in activity just below ground surface. This corresponded with the stratum of organic soil which has acted as a trap for ^{60}Co that was present in the Chemical Pit plume. In performing in-situ leaching, it is expected that the leachant will contact the organic soil in the immediate vicinity of the injection well. However, for most part of the cell, the organic layer was located above the experiment's watertable. As a result, the organic horizon was excluded from inventory calculations, and the conversion of count rates to ^{90}Sr concentrations in this stratum was not performed.

For the sand strata in the test cell, correlations between count rates and the concentrations of ^{90}Sr and ^{60}Co on soils were attempted, using gamma scans from the holes where soil samples had been collected and analyzed, and averaging the downhole count rates over the interval represented by each sample. From that analysis, 80% of the counts detected in the sand were accounted by ^{90}Sr, and for this study, therefore, the scan data should be treated as a reflection of the radiostrontium content in the soils surrounding each borehole. It should be noted that the calculated ^{90}Sr concentrations from the scans were treated semi-quantitatively.

5.3.3 Hydraulic Properties from the Tritiated Water Injection

The injection of leachant began at 14:10 on 1994 August 30, and concluded 16:14 on September 6; the leachant consisted of seven batches mixes of sodium dithionite and tritiated water. The tritiated water added with each batch of sodium dithionite produced an average injection concentration of 255 Bq/min, with a range from 223 to 292 Bq/mL. Rates of leachant supply to the test cell during the sodium dithionite injection phase ranged between 480 and 634 mL/min, with an average of 570±55 mL/min. Taking the thickness of the sands in the test cell to be 2.6 m, and a porosity of 0.40, this injection rate translates into the addition of 1 pore volume of leachant to the test cell in 4.27 days. The tritium and sodium dithionite injection represented the first 1.34 pore volumes of leachant added to the test cell.

One priority in the initial stage was the delineation of tritium breakthroughs in the multilevel samplers, to improve the resolution of the test cell's hydrostratigraphy. Tritium concentrations (relative to the mean input concentration) were measured in samples collected from the 1-m and 2-m depth piezometers at distances of 0.8 m (Bin-2), 1.7 m (Bin-4) and 2.5 m (Bin-6) from the injection well against volume injected, expressed as test cell pore volumes. Also, breakthrough curves were calculated using the analytical solution provided by van Genuchten and Alves [1982].

Dispersivities used in calculations for the analytical model range from 0.2 to 0.3 m, using porosities ranging from 0.40 to 0.45. Apart from the breakthrough curve observed at the 2-m depth in Bin-6, there is reasonable agreement between calculated and observed mass recoveries. The display of tritium measurements was terminated when the concentration of ^{90}Sr began to contribute significantly to the liquid scintillation count rates. The available portion of the withdrawal well curve gave a good fit to the analytical curve for a porosity of 0.40 and a dispersivity of 0.40 m.

The dispersivity values for the test cell were two orders of magnitude higher than the laboratory-scale soil column dispersivities measured using the ES-31 composite sand. The difference between the soil column and field dispersivities may be due to heterogeneity of the soil in the test cell. If layering was reasonably continuous along the length of the test cell, the effects of the heterogeneities will be greatest in the withdrawal well, and indeed the dispersivity determined from withdrawal well is the highest observed in the experiment. Figure A.30 shows the tritium distribution in the test cell at 11:00 on 1994 September 2, after 0.6 pore volumes of labelled water had been injected. The test cell stratigraphic contacts were superimposed on the concentration contour plot. The plot shows that there is slight preferential flow in the medium-fine sands, and also in the oxidized zone contained in the overlying fine sands.

One notable difference between the test cell data and information from the CRL Twin Lake test site [Killey and Moltyaner 1988], however, was that when tracer was added in a pulse and allowed to advect under the Twin Lake site's natural flow field, dispersivities measured at points in the downgradient aquifer were a factor of 10 smaller than the point dispersivities observed in this study. It is suspected, therefore, that much of the dispersivity derived from measurements in the multilevel samplers appears to have resulted because of the test cell geometry, producing convoluted flowpaths in the "dead" ends of the test cell. The significance of this interpretation of the data is that rapid increases in dispersivity are not anticipated in larger-scale soil leaching.

5.3.4 Effect of Addition of Sodium Dithionite

Sodium dithionite solution was added to the test cell along with the 0.57 L/min of tritiated water. The sodium dithionite concentrations ranged between 470 and 1,630 mg/L, with a mean of 930(±350 at 1σ) mg/L (0.005 M). Grab samples of leachant entering the injection well showed solution Eh values ranging from -480 to -540 mV. Despite the evidence provided by the tritium data that the leachant had advected through the entire test cell, there was no substantial decline in redox potentials, either in the withdrawal well or in measurements of samples collected from the multi-level piezometers. Drift and excessive rates of loss of the reference electrode filling solution affected the continuous records of Eh in the withdrawal well, but the electrode was periodically re-filled and calibrated against the Orion reference solutions and point measurements were recorded at those times. The initial redox potential in the test cell's discharge water was +100 mV, and subsequent measurements ranged between +100 mV and -100 mV, with no consistent trend. The same observations were found to apply for results from the multilevel piezometers.

During the first 6 days of the test when sodium dithionite was being added to the test cell, gamma scanning did not reveal significant mobilization of radioactivity in the test cell sands, even at a distance of only 0.35 m from the injection well. Because of the inability to significantly lower the redox potential, and because of the capacity for storing test cell leachate being limited, the addition of sodium dithionite was stopped on 1994 September 6 and the addition of 0.1 mol/L HCl leachant began. At this time, the addition of tritium was halted, so that the trailing edge of the tritium spike would serve as a marker for the leading edge of the HCl addition.

5.3.5 Effects of Acid Addition

(a) pH and Iron

The acid neutralization capacity of sands in the study area has previously been found to be such that 0.4 to 0.5 meq of H^+ ion was needed to reduce the pH of 100 g of sand to 4.5 [Jackson and Inch, 1979]. The very low buffering capacity was due to the low amounts of carbonate minerals in the sands, and the effect of the 0.1 mol/L HCl addition was almost immediately evident. Figure A.31 displays tritium concentrations and pH plotted against injected pore volumes at distances of 0.8, 1.7, 2.5, and 3.1 m from the injection well. Pore water pH dropped from an initial value of around 5.1 in concert with the first arrival of tritium-free injection HCl leachant. At Bin-2 (0.8 m from the source), the pH declined exponentially to a steady-state average value of 1.4, similar to the pH of the added acid. With increasing distance from the injection well, however, a buffering reaction that temporarily held the pH at 3.2 became increasingly evident. In the test cell effluent, after the initial rapid decrease, the pH remained stable at about 3.2 for 1.5 pore volumes of HCl leachant feed, and then decreased slowly towards the feed solution pH. From the quantity of HCl added before the pH fell below the 3.2 value represents an acid neutralization capacity (ANC) of 4.0 meq/100 g of test cell sand, a factor of 10 higher than the pH 4.5 ANC.

Figure A.32 shows pH, and the concentration of Fe in the test cell effluent from the withdrawal well. Concentrations of iron are inversely related to pH throughout the elution stage. It is inferred that dissolution of iron oxyhydroxides represents a major component of acid neutralization capacity which is buffered at a pH of 3.2; if this inference is correct, the calculated iron oxyhydroxide coatings represent 0.1% of unleached sand by weight, assuming a goethite composition. While the pH was buffered at 3.2, iron concentrations were about 140 mg/L in the test cell effluent; as the pH subsequently decreased, iron concentrations rose to about 225 mg/L and remained there until the acid addition was terminated.

(b) Strontium-90

Strontium-90 concentrations in the test cell effluent show a pattern that is consistent with the data on radiostrontium sorption that has been provided by previous studies involving the sequential leaching of sands. The initial, extremely rapid rise in ^{90}Sr corresponds with the first reduction in effluent pH (Figure A.33), and precedes the rise in Fe concentrations (Figure A.32). This is attributed to the release of radiostrontium from ion exchange sites on the soils. Sequential leaching studies [Buckley et. al., 1992] predicted that ion exchange sorption accounted for 30 to 40 percent of the sorbed ^{90}Sr. The leaching tests also predicted that amorphous iron oxyhydroxides accounted for 50 to 60 percent of the total sorbed ^{90}Sr, leaving 10 to 15% associated with crystalline iron oxyhydroxides or strongly retained by other mineral components in the sands. This pattern is supported by the ^{90}Sr release behaviour in the in-situ leaching results. If we consider the dissolution of iron oxyhydroxides to be essentially complete after passage of 3.75 pore volumes of leachant through the test cell (the point at which pH values began to decrease from 3.2), the total inventory of ^{90}Sr removed from the test cell is 175 MBq, out of a total extraction of 187 MBq, i.e.,, 93% of the^{90}Sr removal had occurred by the time the iron oxyhydroxide coatings were leached.

Acid additions were terminated on 1994 September 25, when it was evident that the leachate storage tank would be filled after adding two more pore volumes of solution to the test cell. Since the intent was to flush leachants from the cell before terminating the study, feed to the test cell was switched to fire hydrant water only. Thus, not all of the ^{90}Sr that could have been stripped from the test cell was removed, a consequence of premature termination of the acid additions.

(c) Cobalt-60

The test cell effluent was also monitored for ^{60}Co. Since the initial inventory on the sands was only 3.8 MBq, only limited success was achieved in extracting the sorbed ^{60}Co. The radiocobalt concentrations in the test cell effluent were always extremely low. It was only practical to analyze small (20 mL) volumes of the test cell effluent, and as a result, many of the effluent analyses fell within the 1σ error associated with sample counting and background correction. Using the small-volume method, detectable concentrations of ^{60}Co were first observed in test cell leachate after passage of 0.5 pore volumes - that is, with the leading edge of the tritium-sodium dithionite leachant. Concentrations of ^{60}Co peaked at 0.12 Bq/mL with the arrival of 1 pore volume, and then decreased to undetectable concentrations for the remainder of the test. There was no evidence for any enhancement of ^{60}Co removal by the addition of HCl.

5.3.6 Soil Analyses, During and After Leachant Addition

(a) Strontium-90

The distribution of ^{90}Sr after termination of the leaching test, based on analyses of soils from the Bin-10, 11, and 12 boreholes is given in Figure A.34. As shown in Figure A.28, throughout most of the volume of sand, radiostrontium concentrations were less than 2 Bq/g (54 pCi/g), with slightly higher concentrations near the sand-organic soil interface adjacent to the injection well. The wedge of sand still containing ^{90}Sr adjacent to the withdrawal well was the section of the test cell that was located above the water table during pumping from the test cell (Figure A.28). The high ^{90}Sr concentrations observed at the top of the two boreholes closest to the withdrawal well were due to the presence of some organic soils in the shallowest samples from these locations. The inventory of ^{90}Sr remaining in the test cell was determined from the gridded and contoured data using the same procedures that were applied to determine the starting inventory. This calculation gave a ^{90}Sr residue of 3.89 MBq, or 3% of the initial radiostrontium load.

One key question concerning this residual ^{90}Sr is its future mobility in the flow system. To obtain an assessment of the unleached amount of ^{90}Sr in the soil, composite samples were prepared for each of the post-leaching boreholes, and these were subjected to the hot citrate-dithionite leaching component of the sequential leaching protocol. In the past, it has been inferred that any radiostrontium remaining on the soils after this procedure is either essentially fixed or will at least be released only very slowly over time, possibly by diffusion out of dead-end microcracks in the sand grains. The results of the composite soil analyses and of the citrate-dithionite extraction are summarized in Table B.22.

The starting concentration of ^{90}Sr, averaged over all of the pre-test sand samples, was 9.6 Bq/g (259.5 pCi/g). In the post-experiment composites, the Bin-10 borehole sands contained 1.6 Bq/g of ^{90}Sr and it is 17% of the initial average concentration, while the Bin-12 sand composite (closest to the injection well) contained less than 5% of the average initial ^{90}Sr load. Samples from near the midpoint of the test cell (Bin-11) have a ^{90}Sr concentration that lies midway between these two. It may be concluded that the post-leaching inventory derived from the gridded data set overestimates the radiostrontium removal, and that closer to 10% of the initial ^{90}Sr inventory remained at the end of the test. If this is the case, at the end of the study about 13 MBq of ^{90}Sr still remained on the test cell sands.

Table B.22 also shows the concentrations of ^{90}Sr remaining in the sands after the citrate-dithionite treatment. Because direct counting of sands was employed for these analyses, there were appreciable analytical uncertainties associated with measurements of the leached sands. However, the radiostrontium represented between 30 and 50% of the total ^{90}Sr left in the test cell at the end of the experiment. This leads to an inference that between 2 and 7 MBq of ^{90}Sr may still be relatively easy to remove from the test section of the aquifer.

(b) Cobalt-60

The kriged contours of measurements of ^{60}Co concentrations in soil samples collected from the Bin-10, 11, and 12 boreholes are given in Figure A.29. The post-experiment ^{60}Co inventory provided by this interpolation is 2.0 MBq, or just over 50% of the starting inventory.

The average concentration of ^{60}Co on soil measured in the test cell sands prior to the experiment was 0.27 Bq/g. The radiocobalt concentrations in sands measured after the test, both as the average of measurements of the individual samples and of the composite prepared for each borehole are also given in Table B.22. Results of the two measurements agree to within their limited precision, and again the data suggest that the inventories calculated from the gridded measurements may slightly overestimate radionuclide removal. In contrast to the 50% removal indicated by the pre- and post-leaching gridded data, these measurements suggest no net removal of ^{60}Co near the withdrawal well (or, possibly, a slight increase in soil radiostrontium concentrations). Only near the injection well does there appear to have been a substantial net decrease in ^{60}Co concentrations, to 50 to 60% of the initial concentrations.

Bin-10, 11, and 12 composite sands were re-analyzed for ^{60}Co following the citrate-dithionite treatment. The results and the percentage of the post-experiment radiocobalt that remains on the sands after the leaching are given in Table B.22. Uncertainties associated with these measurements were large and consequently it is speculated that about 50% of the radiocobalt would not be available for release under normal groundwater and geochemical conditions.

5.4 Pilot-scale Ex-situ Soil and Leachate Treatment

5.4.1 Soil Leaching

(a) Approach and Goal

A series of soil leaching tests were performed on pilot-scale to determine the efficacy of radionuclide removals (U from Fernald Incinerator Area soil, and ^{90}Sr, gamma emitters including ^{60}Co and ^{137}Cs and trace levels of uranium from the Chalk River soil) using dilute mineral acid (sulphuric or hydrochloric acid) as the principal leaching chemical with and without ultrasonic mixing. As described previously (section 4.3.3), in the present soil leaching tests, a 10% (w/w) soil-water slurry was pumped from a mechanically agitated head tank to the ultrasonic mixing chamber at a volumetric flowrate of 30 L/min (for soil leaching tests with the ultrasonic tank) and 10 L/min (for tests with the tubular ultrasonic liquid processor).

In the present experimental arrangement, if "total mixing" of the soil-leachant is considered, then ultrasonic mixing is only a small portion of the total mixing (which includes mechanical mixing of the soil-water contained in the head tank at about 1200 rpm and pump mixing in the delivery of the soil suspension to the ultrasonic chamber) imparted to the soil leaching test performed in this study. However, the expectation was that in short contact times (a few minutes) between the soil and the leachant, the role of ultrasonic mixing was to provide micro-mixing effects to enhance uniquely the contaminant removal process.

At the same time, the "macroscopic mixing" effects provided by the pump and mechanical stirring were expected to have very little impact on contaminant removal efficiency at short leaching times, but would have a significant effect on contaminant removal at relatively long contact times (several tens or hundreds of minutes). The expectation was also that for a given particle size of the soil to be treated, the use of lower concentrations of common leachants and leaching temperature should be adequate to achieve the desired contaminant removal efficiency in the presence of low-power ultrasonic fields at short contact times.

(b) Untreated Soil Characteristics

Chalk River Soil

The Chalk River soil was collected from a predetermined location, downgradient of the Chemical Pit, within the premises of AECL's Chalk River Laboratories. The soil obtained was a mixture of soils near the CP-1 and ES-31 locations (Figure A.4). The soils were mixed manually using shovels and rakes in a steel bin and then rotated at 60 rpm in a cement mixer for about 3 minutes. The mixed soil was collected in four 45-gallon drums and shipped to the pilot-scale soil treatment facility.

Sampling of the soil mixture gave average concentrations of 512 pCi ^{90}Sr and 15.8 pCi total gamma/g of soil. The condition of the soil was such that the radioactivity was in between the radioactivity of the soils used in the bench-scale ex-situ soil leaching (1204 pCi ^{90}Sr/g) and in-situ field soil leaching (260 pCi ^{90}Sr/g) tests (Table B.6). The mean particle size of the "as received" soil was 174 μm and the ground soil, which was used as the feedstock for the pilot-scale soil leaching tests, was 79.6 μm (Figure A.35).

Differences in ^{90}Sr Concentration in the Untreated Soils Used in Different Leaching Studies

The Chalk River Chemical Pit soil used in the ex-situ bench-scale leaching tests was significantly different from the soil used in bench-scale column leaching, ex-situ pilot-scale leaching and in-situ leaching tests. The basic difference among the soil samples was that the sample used in the ex-situ bench-scale tests had a relatively high average concentration of ^{90}Sr (1200 pCi/g) and these samples were collected from bore holes CP-1 and CP-4 which are close to the Pit (see Figure A.4); soils used in the pilot-scale ex-situ leaching tests contained 512 pCi ^{90}Sr/g and the soil was taken in the vicinity of the in-situ test cell; in the in-situ field tests the ^{90}Sr content in the untreated soil was 260 pCi/g; and in the bench-scale soil column leaching tests, the soil had an average concentration of 216 pCi ^{90}Sr/g and the soil was taken from bore hole ES-31.

Fernald Soil

Two 45-gallon drums of the untreated Fernald Incinerator Area soil were obtained from the Fernald Environmental Management Project (FEMP) site. The particle size and distribution of the "as received" soil is shown in Figure A.36. The screen analysis showed that the "as received" soil contained over 75% of the particles less than 38 μm diameter and the diameter of about 5% of the particles was greater than 3.35 mm. In the pilot-scale soil leaching tests, the "as received" soil was sieved using a mesh 8 Tyler sieve to separate large particles. The median particle size of the screened soil feedstock was 25 μm diameter. The initial moisture content in the soil was about 5% (w/w).

(c) Chalk River Soil Leaching Results

Scoping Study with Ultrasonic Tank in Recirculation Loop

The amount of radionuclides that was present in the soil used in these tests was about 50% of the radionuclides in the soil used in the bench-scale soil leaching tests (section 5.1.2). Consequently, it was determined to use a 0.1 mol/L HCl solution for the soil leaching tests at a temperature of 30 to 40 °C. The feed soil was mixed with the pre-heated leachate in the head tank. Since the objective was to obtain an overall radionuclide removal behaviour from these soils, a range of leaching times (2 to 60 min) was tested using an ultrasonic tank system as shown in Figure A.8. The soil-leachant suspension (~10 wt% soil) was fed at a flow rate of about 30 L/min to the ultrasonic tank. The residence time in the ultrasonic tank was about 0.5 min. The suspension was recycled back to the head tank in a closed loop to study the effect of total leaching time on contaminant removal efficiency. Sampling of the suspension at predetermined times was made at the outlet of the ultrasonic tank to determine radionuclide content in the soil after leaching.

The effectiveness of soil leaching on the removal of ^{90}Sr and gamma emitters (gross) is shown in Figures A.37 and A.38, and Table B.23. The results suggest that the application of low ultrasonic power input (~470 W) combined with 0.13 mol/L HCl leaching at a slightly elevated leaching temperature (38 °C) and a short leach time of about 3 minutes is sufficient to remove ^{90}Sr and total gamma emitters to meet the target of 35 pCi (^{90}Sr + total gamma)/g of treated soil (or 1.3 Bq/g). The use of higher leach times appears to have no significant advantage in further lowering of contaminant levels in the treated soil.

The relative ease with which the contaminant was removed from the soil was somewhat different from the observed data from bench-scale results. To ascertain this observation, soil leaching tests were performed using the same recirculation flow-loop at a soil-leachant suspension flow rate of 30 L/min without the ultrasonic field. The results given in Figures A.37 and A.38 show that the high suspension flow rate alone is sufficient, within the experimental errors, to remove the contaminants close to the target level even at short leach times. The results also show that in addition to flow and ultrasonic mixing effects, increasing the soil leaching temperature from about 30 °C to about 40 °C has an overall favourable effect of increasing the contaminant removal efficiency.

The initial soil leaching tests in the ultrasonic tank with continuous circulation of the soil-leachant slurry in a recirculation loop indicated that soils with lower ^{90}Sr concentration were easier to leach with low concentrations of HCl (0.1 mol/L) to meet the target of 35 pCi (^{90}Sr + ^{60}Co)/g of treated soil. The higher concentration ^{90}Sr soil used in the bench-scale ex-situ leaching tests required two-stages of leaching to meet the target.

Soil Leaching Results With an Ultrasonic Liquid Processor

The surprising, yet very favourable, contaminant removal results using the ultrasonic tank with or without an ultrasonic field suggested that it may be possible to use much lower leach times and leachant concentrations, and possibly at lower leaching temperatures (e.g., 20 to 25 °C) to achieve the target quality for the treated soil. This prompted the leaching tests to be carried out in a tubular liquid processor, in which the leach contact times were 0.03 to 0.07 min. The soil slurry was pumped at a flow rate of 10 L/min.

The leachant injection was made to the slurry stream just prior to entering the ultrasonic cavity. The exiting slurry was dewatered continuously by the filterpress (see Figure 9) slurry was not recirculated. The flow rate used in this test was about one-third of the flow rate used in the scoping tests described previously with the ultrasonic tank system. The results are presented in Table B.23 and in Figure A.39.

Single-stage leaching results showed that water leaching alone removed about 39% ^{90}Sr, whereas about 87% of ^{90}Sr was removed by leaching with 0.05 and 0.13 mol/L HCl solutions. A two-stage leaching (with 0.13 mol/L HCl in first stage and 0.1 mol/L HCl in the second stage) showed about 87% ^{90}Sr was achieved in the first stage and only about 46% of the remaining radiostrontium was extracted from the soil in the second-stage leaching. The data indicated that the contaminant removal became progressively more difficult to remove using the same leachant concentration.

In terms of treated soil concentration, the single-stage leaching with 0.05 mol/L HCl gave a value of about 3.1 Bq ^{90}Sr/g of soil (~84 pCi/g) and 0.13 mol/L HCl gave a value of about 2.44 Bq/g (~66 pCi/g). A second-stage leaching could reduce the final activity to 1.89 Bq/g (51 pCi/g). The gross gamma values in the treated soil varied in the range of 0.3 to 0.36 Bq/g (~ 8 to 10 pCi/g).

The results clearly show that increasing the acid concentration over about 0.05 mol/L has beneficial effects, but the effect is not significant. For example, a 60% increase in the acid concentration from 0.05 mol/L gave only about 20% reduction in ^{90}Sr concentration in the treated soil. The results also show that increasing the leaching temperature provides beneficial effects. For example, the residual ^{90}Sr concentration reduced from 4.37 Bq/g to 3.15 Bq/g, when the leaching temperature was increased from 10 to 26 °C. To achieve the target of 1.3 Bq (total beta and gamma) per gram of treated soil, some variables may have to be changed either individually or in combinations. For example, a slight increase in temperature (from 25 °C to 30 °C), or increase in contact time (from 0.03 min to 0.1 min by addition two more ultrasonic liquid processor, or using a single ultrasonic processor with reduced slurry flow rate), or the addition of a reducing agent such as sodium dithionite to the acid solution should be sufficient to achieve the target.

Indications from the pilot-scale once-through soil leaching results for ^{90}Sr removal with water alone prior to acid addition (Tables B.24 and B.25) prompted additional bench-scale water leaching tests with an ultrasonic field and also with mechanical agitation in the absence of an ultrasonic field. The experimental arrangement is identical to the procedure described in sections 4.1.1 and 4.3.3. The bench-scale results are given in Figure A.40. The results show at short contact times (10 to 20 seconds), ultrasonic-aided water leaching removed 30 to 48% of ^{90}Sr, whereas mechanically-agitated mixing removed 20 to 30% ^{90}Sr but at much higher contact times (30 to 60 minutes). In general, the use of excessive contact times resulted in virtually no removal of ^{90}Sr for ultrasonic and mechanical water leaching of the Chalk River soil. This unexpected results suggest that prolonged contact of the soil after leaching with the leachate may induce a re-adsorption process, particularly when the released ^{90}Sr is not chemically complexed in the leachate solution.

(d) Fernald Soil Leaching

A series of pilot-scale ex-situ soil leaching tests was performed with the Fernald Incinerator Area soil to determine the effectiveness of uranium removal under different processing conditions. A summary of the test conditions and results is presented in Tables B.29 and B.30, respectively. Test F1 involved water leaching alone at room temperature. Tests F2 and F3 were conducted to examine uranium removal efficiency with and without an ultrasonic field using dilute sulphuric acid as the leachant. Test F4 involved 0.25 mol/L sulphuric acid leaching at 40 °C with the addition of 0.03 g $KMnO_4$ per gram of soil as the oxidant for uranium (IV) to U(VI) conversion. The selection of sulphuric acid and $KMnO_4$ was based on the most promising results from the bench-scale leaching tests (section 5.1.2). Test F5 used a 0.2 mol/L alkali leaching ($NaHCO_3$ + Na_2CO_3) to assess the effectiveness of the process with similar conditions employed previously [Francis, 1994] at the Oak Ridge National Laboratory. Soil leaching Tests F6 and F7 were conducted to evaluate the effect of ultrasonic field on uranium removal efficiency using 0.23 mol/L sulphuric acid with 0.03 g $KMnO_4$/gram of soil at 40 °C. Detailed data for Tests F4 and F6 are given as examples in Tables B.31 and B.32, respectively. Test F8 was conducted to study the residual uranium profile in the treated soil using dilute sulphuric acid at 42 °C. The soil-leachant slurry was pumped through the ultrasonic cavity using single-pass mode without circulation.

The soil leaching test configuration is given in Figure A.10. All tests involved the use of the tubular ultrasonic liquid processor. In addition to this slurry mixing was achieved by a mechanical agitator in the head tank and the soil-water slurry was delivered to the ultrasonic processor by a double-diaphragm pump. For tests without the ultrasonic field, the equipment arrangement was identical except that the ultrasonic power was not turned on. A soil batch of about 30 kg was used for each test. In a typical test, the soil-water slurry was pumped in a recirculation loop via the ultrasonic liquid processor. The leachant and other chemicals, as applicable, was injected in-line and the exiting slurry from the ultrasonic cavity was discharged back to the head tank. Because of this arrangement, the very first sample taken outside the ultrasonic system would represent a once-through condition. At the 40 L/min soil-water slurry flow rate used, a total time of about 8 min would represent the time required to deliver the full batch of slurry from the head tank via the ultrasonic processor.

In Tables B.31 and B.32, the "circulation time" represents the actual time the soil-leachant slurry was in the loop including the head tank. The final concentration of uranium reported for the "treated" soil represents the final value in the wet cake corresponding to the total time (circulation, filtration and washing).

The Fernald soil leaching posed a number of experimental problems. As the soil contained mainly fine particles with "sticky" characteristics, delivery of the soil-water slurry using the diaphragm pump was a problem as a result of frequent pump seizure and plugging of pipe bends. For this reason, the soil-water flow rate had to be maintained very high (about 40 L/min). The dewatering of the treated soil by the plate-and-frame filter press was also difficult because of frequent filter-cloth blinding issues. As a result, the filtration rate had to be reduced considerably.

Furthermore, a small amount of a filter-aid (Harborlite, Table B.4) at concentrations in the range of 4 to 5% (w/w) of the soil batch was required. Generally, the filtration time was very high. The sulphuric acid-soil system took about 150 minutes to dewater, but when potassium permanganate was present the filtration time was reduced, by a factor of 5, to 30 minutes. The alkali-soil system showed very poor filtration performance taking about 750 minutes to filter the volume of liquid.

Because of the high slurry flow rate usage (40 L/min), there was a concern that this high flow rate may generate sufficient mixing of the soil-leachant solution, which would ultimately surpass the contribution by the ultrasonic field to contaminant removal enhancement.

Uranium Removal Results Based on Final Treated soil (or Wet Cake from Dewatering) corresponding to Maximum Reaction Time for Soil Leaching

The results given in Table B.30 (column F) show that water leaching alone removed only about 10% of uranium (TSQI = 9.5). Dilute sulphuric acid (~0.1 mol/L) leaching without the addition of potassium permanganate gave a TSQI value of 3.9 using only flow mixing and mechanical agitation in the head tank feeding the soil and water slurry. A slight increase in acid concentration combined with the superposition of an ultrasonic field reduced the TSQI to 1.6, a value above the desired target.

A further increase of acid concentration to 0.25 mol/L with the simultaneous addition of potassium permanganate in the presence or absence of an ultrasonic field at about 40 °C resulted in TSQI values that exceeded the target TSQI value of 1 for the treated soil. Results for $NaHCO_3/Na_2CO_3$ (0.2 mol/L each) leaching was poor. The TSQI value of 3.8 obtained from the alkali leaching was comparable to 0.1 mol/L sulphuric acid leaching at room temperature in the absence of potassium permanganate and an ultrasonic field.

These above results suggested that given sufficient leaching time, the combined action of 0.23 to 0.25 mol/L sulphuric acid and potassium permanganate (about 0.03 g/g of soil to give 1100 to 1200 mV for Eh) at a leaching temperature of 40 °C is sufficient to meet or exceed the target value of 35 pCi uranium/g of treated soil (52 mg U/g of soil). To achieve this result, the fundamental requirement is that sufficient soil-solution mixing is needed, although there was no evidence of any specific requirement for the use of ultrasonically-aided leaching. It should be, however, noted that in these tests even without the use of an ultrasonic field, sufficient mixing was provided in the recirculation loop by the slurry delivery pump delivering the slurry at 40 L/min and the mechanical agitation provided in the head tank holding the slurry.

Uranium Removal Results at Intermediate Reaction Times (Table B.30, columns C, D and E)

As the reaction time for soil leaching is reduced, the TSQI values corresponding to each test condition increased, as expected. The differences among the TSQI values for a given test condition was found to be relatively large, when sub-optimal condition for reagent type and concentration, and temperature was used.

Uranium Removal Results at Low Reaction Times, Corresponding to Once-through exposure to ultrasonic field (Table B.32, column B)

The uranium removal results given in column B (Table B.32) corresponds to about 1 second reaction time between the soil and the leachant. A comparison of the results for Tests F4 and F7 involving an ultrasonic field suggests that the majority of uranium removal occurs in an extremely low contact time of about 1 sec. For the control test (Test F6), without the ultrasonic field, the magnitude of flow mixing employed as a result of 40 L/min flow was also surprisingly effective in uranium removal, although the uranium concentration in the treated soil was about 20% higher than the result obtained with the ultrasonic field present. It is anticipated that at low slurry flow rates that would be normally used in practice, the difference between "with ultrasonic" and "without ultrasonic" fields on contaminant removal would be amplified.

A conceptual diagram for soil leaching kinetics involving short and long contact times is shown in Figure A.41. With reference to the figure, it appears from the results examined thus far that low-frequency ultrasonic energy should only be utilized for the initial portion of the reaction domain, where the contaminant is removed in an accelerated fashion. The remaining portion of the reaction domain contributes to the slow removal of the contaminant, although it is equally important, in meeting the overall target for soil treatment. Since soil slurries such as produced by Fernald Incinerator Area soil take relatively long times (several tens of minutes) to dewater, the dewatering time may be effectively utilized in achieving the final uranium removal necessary to meet the target value for treated soil.

Carbonate-Bicarbonate Soil Leaching for Fernald Incinerator Area Soil

The carbonate-bicarbonate leaching of soils is generally performed in the pH range of 9 to 9.5. The leachants are added as salts of sodium or ammonium. The role of bicarbonate is to neutralize the hydroxide ions produced during leaching. This leaching procedure is commonly referred to as "carbonate leach". The use of carbonate leach requires the use of an integrated closed circuit process, wherein the leach solutions are recycled and the reagents are reused.

The carbonate leachate is nearly selective for dissolution of uranium from soils, and compounds of iron and aluminum are generally not leached because of poor solubility in carbonate solution. Uranium removal occurs through the formation of highly soluble anionic carbonate uranyl species, including uranyl dicarbonate and uranyl tricarbonate.

Carbonate leach has been used to recover uranium from ores [Merritt, 1971], although this process is not used currently. The majority of uranium recovery processes world-wide employ presently sulphuric acid leaching of ores.

Recently, Los Alamos and Oak Ridge National Laboratories have employed carbonate leach for Fernald soils [LANL, 1994; ORNL, 1993a]. By simulated heap leaching in column experiments [LANL, 1994], about 70 to 90% of the uranium has been removed from the Fernald Storage Pad soil after ten days of leachant (0.25 mol/L $NaHCO_3$ + 0.25 mol/L Na_2CO_3 solution) percolation.

The Oak Ridge Study [ORNL, 1993a] on carbonate leaching of Fernald soils has shown uranium concentrations in the treated soil of 89 mg/kg for the Storage Pad soil and 215 mg/kg for the Incinerator Area soil. The study recommended carbonate leach as a pretreatment method to remove uranium from specific size fractions of the soil.

A supplementary study of carbonate leach [Francis, 1994] with Fernald incinerator soil shows uranium removal efficiencies in the range of 80 - 84% by pilot-scale leaching with a mixture of 0.25 mol/L bicarbonate and 0.25 mol/L carbonate solutions. The best data obtained in their study indicate uranium concentrations between 100 and 175 mg/kg in the treated soil.

However, the composition of other elements leached during the process, and the amount of soil dissolved have not been reported. The heap leaching study [LANL, 1994] using carbonate solution on Fernald Storage Pad soil report iron concentrations in the order of 500 mg/L in the soil leachate. This suggests that carbonate leach may not be as selective as has been expected. Also, a finite amount of the soil is likely to dissolve during leach.

Bench-scale leaching results (Table B.12) from the present study show that uranium concentrations from the Fernald Incinerator Area soils can be reduced to 170 mg U/kg by a mixture of 0.3 mol/L Na_2CO_3 and 0.3 mol/L $NaHCO_3$ solution. The soil leaching also dissolved about 4 % (w/w) of the soil at a soil to leachant ratio of 1 to 10. These results were obtained with ultrasonically-aided mixing for 3 minutes at 50 °C. Our pilot-scale tests using a recirculation mode leaching (soil to leachant ratio = 1:10; $[NaHCO_3 + Na_2CO_3]$ content of 0.4 mol/L) show a reduction of uranium concentrations in the soil from 600 mg/kg to 300 mg/kg in about 7 min of leaching and gradually to 220 mg/kg after 15 to 30 minutes.

All of the above results suggest that the use of carbonate leach to remove uranium from the Fernald Incinerator Area soil will not produce a treated soil that meets the target value of 35 pCi U/g of soil (or 52 mg U/g of soil).

In summary, selected pilot-scale data presented by Francis [1994] indicate that, at best, a residual uranium concentration in the range of 100 to 175 mg/kg (67 to 134 pCi/g) can be obtained using multi-stage attrition leaching, with reagent recycle at leachant concentrations between 0.25 and 0.5 ml/L each of $NaHCO_3$ and Na_2CO_3 and possibly at a leaching temperature of 40 °C.

It should be noted that our bench-scale results have shown residual uranium concentrations of about 100 mg/kg can be easily obtained with 0.1 mol/L H_2SO_4 in the presence of small amounts of an oxidizing agent (air or $KMnO_4$) with a soil to liquid ratio of 1 to 10 at 40 to 50 °C. The leaching temperature was achieved by heating the leachant to the desired temperature and maintaining it using a temperature controlled hot-plate system. For similar conditions, our pilot-scale results suggest that slurry flow mixing for leaching times of 15 to 30 minutes can reduce uranium in treated soil to below the target value of 52 mg/kg of soil.

5.4.2 Soil Leachate Treatment

(a) Approach and Goal

Leachate treatment was performed to remove contaminants and other metals efficiently using a combined chemical precipitation/sorption method in the presence of an ultrasonic field coupled with flow mixing. The goal was to produce a treated leachate that can be either discharged or recycled back to the soil treatment plant. The soil leachates generated from soil leaching of the Chalk River and Fernald soils contained high amounts of dissolved solids (Tables B.26 and B.33) primarily resulting from the anions and the alkali and alkaline earth metals.

Consequently, although the primary contaminants (U, ^{90}Sr, etc.) can be removed effectively, the secondary contaminants including sulphate (from Fernald soil leaching) and chloride (from Chalk River soil leaching) must be dealt with. The treated leachate from Chalk River soil leaching contained 4,000 to 4,500 mg/L of total dissolved solids (TDS) and treated leachate from Fernald soil leaching contained TDS values in the range of 2,800 to 24,000 mg/L, depending on the type of chemical reagents employed for leachate treatment.

On the basis of bench-scale leachate treatment results (section 5.1.3), we selected a soda-lime precipitation process as the main method, followed by zeolite sorption as the polishing step for the treatment of Chalk River soil leachate. For Fernald soil leachate, we employed different precipitants ($NaOH + H_2O_2$, lime + H_2O_2, magnesia + H_2O_2) with or without the addition of ferric chloride as the flocculant/ion-scavenging agent. The application of different precipitants was triggered primarily by the goal to minimize the amount of secondary waste generation in the leachate treatment as wet cake. The result was that for a given uranium removal efficiency, high TDS in the treated leachate correspondingly gave a low volume of secondary waste.

The leachate volumes treated consisted of batches of 400 to 800 litres. Three test modes were employed. The first test mode was used for all Chalk River soil leachate tests (Tables B.27 and B.28). In this mode, the precipitant and other chemicals were added directly to the head tank containing the leachate batch. Following this step, the solution was pumped through the tubular ultrasonic system and back to the head tank in recirculation loop. The recirculation mixing continued for predetermined treatment time. The treatment flow rate was in the range of 5 to 15 L/min. There was no mechanical agitation provided in the head tank. Samples were taken at fixed times from the recirculation loop for chemical and radiochemical analyses. At the end of the test, the suspension from the head tank was dewatered in the filterpress. When ultrasonic power was not needed, the power was turned off, but the same recirculation loop was used. These tests were performed to demonstrate that the overall process chemistry was effective in removing the contaminants and may be considered as near equilibrium mixing condition for precipitation.

The second and third test modes were applied for Fernald soil leachate treatment. Similar to the first test mode, the chemical reagents were added to the head tank containing the leachate batch to be treated. Following this step, the mixture was pumped in a single-pass via the tubular ultrasonic processor. The exiting suspension was continuously dewatered in the filterpress. It should be noted that this mode of testing did not involve recirculation of the suspension back to the head tank. Samples were taken just outside of the ultrasonic system and analyzed for metals, anions and total dissolved solids. The third and final test mode was performed by in-line injection of the chemicals to the untreated leachate stream flowing from the head tank in a single-pass via the tubular ultrasonic system and to the dewatering equipment. The precipitate suspension exiting the ultrasonic system was continuously filtered by the filterpress, and samples of the filtrate and suspension were taken for chemical analysis at predetermined times.

(b) Untreated Leachate Characteristics

The assays for untreated soil leachates (feed composition) for the different batches tested are given in Table B.26 for the Chalk River soil leachates and in Table B.33 for the Fernald soil leachates. The assay includes the composition of the primary contaminants and selected metals, and total dissolved solids.

The concentration of gamma emitters in the Chalk River leachate feed was essentially at the method detection limit and therefore not monitored further. Strontium-90 concentrations varied in the range of 500 to 1,400 Bq/L. Uranium was found to present in low concentrations (0.02 to 0.9 mg/L). The TDS varied over the range of 1,000 to 13,000 mg/L.

The Fernald soil leachate contained uranium in the range of 20 to 35 mg/L. The TDS varied from about 5000 to 19,000 mg/L. The majority contribution to the TDS resulted from the use of sulphuric acid as the leachant. The sulphate concentration ranged from about 9,000 to 22,000 mg/L.

(c) Chalk River Soil Leachate Treatment by Precipitation/Sorption

Similar to soil leaching results, lime-soda precipitation in a single-stage contact using long contact times (greater than 70 min) in a recirculation loop with flow and ultrasonic mixing was sufficient to reduce ^{90}Sr concentration to below 10 Bq/L (270 pCi/L). The inclusion of a second-stage with chabazite and MnO_2 additions to remove residual ^{90}Sr from the first stage did not produce any beneficial effects.

A detailed examination of the test results (for example, Test CL5, Table B.27) revealed that much lower contact times (15 min) for precipitation was sufficient to produce the same removal efficiencies as higher contact times (45 min or greater). Similarly, other metals including iron, calcium and uranium were also removed effectively by the treatment process. However, the final total dissolved solids in the treated leachate was relatively high (4,000 to 5,000 mg/L) because of the presence of chloride ions from the HCl leachant, and metals such as calcium and sodium resulting from the precipitation chemicals used.

(d) Fernald Soil Leachate Treatment by Precipitation/Co-Precipitation

A summary of results for Fernald leachate treatment with different precipitation chemicals is given in Table B.30. Detailed data for selected tests are given in Tables B.34 and B.35.

For soil leaching by H_2SO_4, the leachate is treated with an alkali to a pH of ~9 to precipitate uranium as alkali diuranate.

For soil leaching by carbonate-bicarbonate (at 0.3 mol/L each), the uranium containing leachate has a pH around 9 to 9.5. To recover uranium from the leachate, firstly, the carbonate ion should be removed to break the strong uranium carbonate complex. This is achieved by the addition of sulphuric acid to a pH of about 3, followed by steam heating to expel CO_2 from the solution. Subsequently, the solution is subjected to uranium precipitation with an alkali such as MgO, ammonia or NaOH in the pH range of 6.8 to 8 [Meritt, 1971].

The disadvantage with lime addition is that it would produce a large amount of precipitate, primarily due to precipitation of sulphate as gypsum ($CaSO_4$). This problem is tackled by performing the uranium precipitation with relatively expensive alkalies such as MgO, NaOH or ammonia.

When uranium concentration in the leachate is low (less than 100 mg/L), in addition to alkali, a co-precipitant (e.g., H_2O_2) and a flocculant/scavenger (ferric compound) is needed to bring the uranium concentration in the final water to drinking water standards (60 µg U/L).

The amount of total dissolved solids (TDS) in the treated leachate can range from about 3000 mg/L to 10,000 mg/L. For soil treatment based on dilute acid leach, the concentration of sulphate as compounds of sodium, magnesium or calcium may amount to 25,000 mg/L (associated with Na or Mg) to 2,000 mg/L (associated with Ca).

The results demonstrate that uranium removal using NaOH or $Mg(OH)_2$ in the presence of a co-precipitant (H_2O_2) and an ion scavenger (Fe^{+3}) is the best choice for leachate treatment primarily because of the relatively low amount of secondary waste generated by the process in comparison with the lime-H_2O_2 process. The use of very low contact times (about 4 seconds) for precipitation and ion-scavenging was sufficient to remove in excess of 99% of the uranium, manganese and iron. An increase of uranium concentration with time (from 0.05 mg/L to 0.28 mg/L) in Table B.35 was due to a loss of efficiency in the dewatering equipment. A suitable selection of filteraid and optimal operation of the dewatering equipment should eliminate this concentration rise. The only drawback was that the total dissolved solids (TDS) in the treated leachate was high (about 12,000 to 24,000 mg/L). It appears that a further optimization of the caustic precipitation process should provide a final TDS value of about 10,000 mg/L.

Evidently, the sulphate levels in the treated water would have to reduced by a polishing step based on ion-exchange combined with evaporation and crystallization, or by biodegradation steps, prior to discharge. This problem is not present with carbonate leach system. The treated leachate can be recycled back to the leach step. The treated leachate containing high concentrations of TDS (as Na_2CO_3) would require infrequent discharges. For this, an evaporation/crystallization step or steam-aided acidification to drive off CO_2 as a method to reduce the TDS value may be implemented.

5.5 Secondary Waste Considerations and Management

5.5.1 Type of Secondary Waste Resulting from Soil Treatment

In the present project, soil treatment is achieved by chemical leaching of the contaminated soil with enhancement fields including ultrasonic mixing and thermal heating to remove contaminants efficiently. Following the soil-leaching step, the treated soil is separated from the contaminant-bearing leachate solution with concomitant water washing. If the treated soil meets the target soil quality for discharge, the soil is released to the environment, either as wet solid or as treated-soil/water suspension.

The separated soil leachate is treated chemically with enhancement fields, similar to soil treatment, to remove the contaminants efficiently though a combination of precipitation/ion-scavenging/sorption steps, followed by dewatering of the contaminant solids (wet cake). The separated treated water is further processed by a polishing step, if necessary, prior to either discharge to the environment or recycle in the soil treatment process.

The contaminants separated as wet cake from the leachate constitute the secondary waste. The goal is to minimize the amount of the secondary waste because management of this waste can increase significantly the cost of soil treatment.

Evidently, there is much incentive to devise cost-effective options to deal with the secondary waste. In some instances, the recovered contaminant(s) contained in the waste can be reused as a resource. In other instances, it has to be handled as a waste and processed further to produce a stable wasteform through appropriate solidification steps, prior to disposal.

The treatment of Fernald soil and the Chalk River soil has resulted in two types of secondary wastes, as determined by the nature of the contaminants originally present in the soil. The Fernald soil contains uranium (long half-life alpha emitter) as the sole contaminant, whereas the Chalk River soil contains short half-life beta and gamma emitters [^{90}Sr (28.8 a); ^{137}Cs (30 a); ^{60}Co (5.3 a); ^{106}Ru (~1 a); and trace levels (3 to 8 ppb) of uranium (^{238}U, 4.5×10^9 a; ^{235}U, 7.1×10^8 a)].

In the analysis below, a consideration of utilization potentials for these wastes has led to two management options. The secondary waste from Chalk River soil treatment will be examined as "waste" appropriate for disposal, and the waste arising from Fernald soil treatment will be examined as "resource", appropriate for reuse in uranium ore milling operations.

5.5.2 Potential Wasteform for ^{90}Sr-Containing Secondary Waste Produced from Chalk River Soil Treatment

The only secondary waste produced as a result of Chalk River soil treatment comes from the soil leachate treatment step as wet cake. The wet cake consists of precipitates of metals and radionuclides, primarily present as carbonate and hydroxide compounds, and sorbents bearing adsorbed contaminants. For the soda-lime precipitation process, the amount of secondary waste generated was found to be dependent on the amount of lime added to the treatment to achieve the desired removal target.

Selected results for the amount of secondary waste produced from pilot-scale tests, together with the concentration of radionuclides in the secondary waste are given in Table B.36 The results show that the weight of the secondary waste (on dry weight basis) is 5 to 10% of the weight of soil leached. For a ton (2000 pounds) of soil treated, the secondary waste amounts to 100 to 180 pounds, depending on the treatment condition. The residual ^{90}Sr concentration in the treated water for these test results is about 265 pCi/L. The total radioactivity in the secondary waste can vary in the range of 2 micro-curie/pound to about 4 micro-curie/pound of dry secondary waste.

It should be noted that the above waste amount does not include filter-aid employed in the dewatering step. Since we added excessive amounts (about 1.2 kg per batch of 400 to 600 liters of leachate treated, or about 40% of the weight of secondary waste dewatered) of the filter-aid on an arbitrary basis, this amount of waste was not included in the secondary waste analysis. In actual operation, however, the amount of filter-aid usage would be limited to about 1% (typically about 0.2 to 0.5%; in special situations up to 4% max.) of the weight the secondary waste being dewatered [Dickey, 1961; Basso, 1977]. Consequently, the weight of secondary waste reported above would increase by about 1% (to a maximum of about 4%).

Leachability Index

Three dynamic leach tests were performed to determine the leachability index and its variance. The test results are shown in Table B.37. The leachability indices for the contaminants concerned were calculated by the equations described in section 4.3.2. The mean leachability indices for ^{90}Sr, ^{60}Co, ^{137}Cs, ^{106}Ru, and ^{241}Am are 10.7±0.12, 12.8±0.12, 12.2±0.42, 9.2±0.0, and 10.9±0.12, respectively. All the leachability indices are greater than the target value of 6 specified by USNRC[1991]. Environment Canada [Environment Canada, 1989] used a mathematical model to predict the amount of contaminant leached from the solidified waste as a function of time. They reported that less than 20% of the contaminant will be leached from the waste in a 100-year period with a leachability index of 10.5, and less than 5% will be leached in 100 years with a leachability index of 12.

The equation for the effective diffusivity is only valid for the case when less than 20% of a leachable species is removed at time t. The amounts of contaminants leached from the solidified waste form tested in this study ranged from 0.1 to 2.5% after a 5 day interval. Therefore, the error introduced from the effective diffusivity equation is insignificant.

The ANS 16.1-1986 leach test is intended to serve for quality assessment purposes and as a basis for comparing the leachability of solidified waste forms under one set of prescribed conditions. If all the initial and boundary conditions for the diffusion model used are met, the leachability index would be independent of time. However, the measurement of leachability index usually includes experimental errors and uncertainty. Therefore, confidence range and correlation coefficient of the leachability index are used as measures of these discrepancies [ANS-16.1, 1986].

The 99.9% confidence range of the leachability index is determined by:

$$CR = L_i \pm 4.781 \sigma_L n^{-1/2}$$

where CR is the 99.9% confidence range of L_i, L_i is the mean of L_n, L_n is the leachability index as calculated from the data of the nth leaching interval, σ_L is the standard deviation of L_n and n is the number of leaching data. The calculated results given in Table B.34 show that the lowest limits of the 99.9% confidence ranges of the leachability indices are also greater than 6. Thus, it can conclude that the product waste form tested in this study meets the performance criterion for leach test specified by the USNRC for disposal.

The correlation coefficient between leachability index and time is defined as:

$$r = \frac{\sigma_{Lt}}{\sigma_L \sigma_t}$$

where r is the correlation coefficient, σ_L is the standard deviation of L_n, σ_t is the standard deviation of t_n, t is the cumulative leaching time, and σ_{Lt} is the covariance of the sets of L and t. The correlation coefficient varies from -1 to +1. The sign indicates whether L_n is tending to increase (+r) or to decrease (-r) as leaching time increases. All the correlation coefficients for the contaminants of interest (Table B.37) are positive values (ranged form 0.08 to 0.86) except for ^{90}Sr (-0.68).

Unconfined Compressive Strength

The compressive strength was measured for 5 random waste samples with a waste to cement ratio of 1 to 1 by weight. The results are presented in Table B.38. The average compressive strength of the 5 samples is 2,084 psi with a variance of 847.6 psi. The mean compressive strength of the tested waste form is about 4 times higher then the recommended performance criterion (500 psi) by USNRC [1991].

5.5.3 Utilization of Uranium-Containing Secondary Waste Produced from Fernald Soil Treatment

The Fernald Incinerator Area soil contains only uranium as the primary contaminant. Isotopic analysis of the soil gives a ^{235}U to ^{238}U ratio of 0.0068 to 0.0071, which is close to the isotopic ratio of 0.0073 found in natural uranium. The uranium concentration in the soil varies from 470 to 605 mg/kg. The only significant heavy metal found was lead at concentrations in the range of 34 to 39 mg/kg. A report [LANL, 1994] suggests that uranium is primarily as U_3O_8, UO_2 and UF_4 in the soil.

The amount of secondary waste produced from leachate treatment is dependent on the type of precipitation reagents employed to remove the contaminant. Selected results are given in Table B.39.

Depending on the chemicals used in the precipitation and recovery of uranium from the soil leachate, several options emerge. The differences among the options are reflected in the differences in quality of treated leachate, and the quantity of secondary waste (wet cake containing about 40% w/w dry solids) produced requiring packaging and shipment to a uranium milling plant for reuse. Presently, this option may not be feasible in the U.S. because there are essentially no plants in operation for uranium mining and milling. However, as a resource, the recovered uranium containing secondary waste should qualify for reuse in the existing uranium milling operations in Sakatchewan, Canada.

A brief description of a typical uranium milling process is given below. The mined ore (uranium concentrations of 0.1 to 1 wt. %) undergoes crushing, grinding and leaching. Finally uranium is recovered as yellow cake from the leachate by precipitation or by solvent extraction combined with precipitation [Hester, 1979; Nirdosh and Muthuswami, 1988] In Canadian milling operations, depending on the uranium content and its distribution in the ore, the ore is ground to 50 % minus 200 mesh or 70 % plus 150 mesh, or 100% minus 32 mesh. The sulphuric acid leaching of the ground ore is carried out in multi-stage atmospheric and pressure leaching tanks at 70 to 75 °C over a leaching period in the range of 5 to 35 hours. The resulting soil-leachate suspension is washed and separated in a series of countercurrent decanters. The washed solids are neutralized with lime and sent to the tailings management area. The separated leachate (containing uranium) from the countercurrent decanters is filtered and then treated either by ion-exchange or by solvent extraction to concentrate and recover uranium. The resulting uranium-rich aqueous solution is subjected to precipitation with ammonia or magnesia to obtain uranium as yellow cake (diuranate of ammonia or magnesia).

As given in Table B.39, the concentration of uranium in the secondary waste (on a dry basis) varies from about 0.1 % (w/w) to 1 % (w/w), depending on the type of precipitant employed. [Note that the use of carbonate leach would produce as high as about 10 % U containing wet cake].

As uranium milling involves uranium content in the ore (dry basis) of 0.1 to 2 wt%, differences in the uranium content in the secondary wet cake should not pose any problem in the reuse of the secondary wet cake in uranium milling. However, the amount of wet cake to handled is significantly different, depending on the type of leachate and precipitant employed to generate the secondary waste.

The cost of handling and shipment of the secondary waste as wet cake (containing ~60% moisture) will be the highest for acid-leaching of soil combined with leachate treatment by lime addition (~2 drums per ton of soil treated), and the lowest for carbonate-leaching of the soil combined with leachate treatment with caustic addition (~0.03 drum per ton of soil treated). Considering secondary waste production and its management, the carbonate leach is the preferred treatment route. This observation is in agreement with the results obtained at Oak Ridge National Laboratory [ORNL, 1993a; Francis, 1994]. However, the carbonate leach cannot produce a treated soil to meet the target uranium concentration of < 52 mg/kg or, < 35 pCi/g of soil. The ORNL treated soil results indicate a range between an optimistic value of 100 mg U/kg with a pessimistic value of up to 220 mg U/kg are achievable.

The use of sulphuric acid (about 0.25 mol/L solution) in soil leaching, coupled with sodium hydroxide addition for leachate treatment, meets readily a target value < 52 mg U/kg of treated soil with a modest amount of secondary waste (~0.3 drum per ton of soil treated) having characteristics suitable for reuse in uranium milling plants. For example, an amount of 2,000 pounds of Fernald Incinerator Area soil when treated on site at Fernald, Ohio will produce as low as 70 pounds of dry secondary waste using a $NaOH-H_2O_2$ process or about 175 pounds of wet cake (~60% moisture). This waste would have to be packaged and shipped over a distance of about 1,500 miles for reuse at the Cluff Lake uranium milling plant in Saskatchewan.

Based on the assumption that the soil can be disposed of without treatment at Envirocare's Utah facility, the amount of 2,000 pounds (~3.3 drums) of untreated soil would have to be packaged and shipped over a distance of about 1,500 miles. This suggests that treating the soil is expected to reduce the cost of packaging and shipping by about 90 % in comparison with the cost of packaging and shipping the untreated soil. The secondary waste reuse in the uranium mill should not incur any significant additional cost.

In the overall cost analysis (section 5.6.1) a significant cost contribution will come from the cost related to the disposal of untreated soil in one case and the treatment cost for the other case.

5.6 Overall Soil Treatment Technology Evaluation

Contaminants can be encountered in both unsaturated and saturated soils. Spills, waste burial, or declining water tables can all lead to unsaturated zone contamination. In most cases, excavation and treatment would be the preferred option, but there are some situations (e.g. overlying wastes or structures, or great depth to the contamination) where the initial step might be to flush the contaminants into the saturated zone or to saturate the contaminated materials by raising the water table. Under saturated conditions, excavation is frequently difficult, especially in the relatively permeable materials to be found where appreciable subsurface contaminant migration has taken place.

If the process does not enhance desorption, experience has shown that cleanup may require extended operation at very low removal concentrations, or periodic pumping with soaking intervals to allow re-establishment of concentrations approaching equilibrium. A choice of chemical conditions which promote selective release of only the contaminants, and not other soil constituents, is obviously desirable.

The transported water containing the dissolved or dispersed species requires processing to produce a concentrated contaminant stream. Again, selectivity can be a major advantage by discriminating between the offending materials and those of no consequence since it reduces the waste volumes and perhaps the reagent costs. One of the major challenges of the development work is to get a suitable match between those mechanisms promoting release from the soil and those utilized in the concentrating step. The approach may be different depending on whether remediation is to be done in-situ or by ex-situ treatment of soil that has been excavated. Both will involve aqueous processing.

The total approach taken by AECL to remove soil contaminants has a number of advantages. First, the various unit operations are straight-forward, the equipment is simple to operate, robust and compact making the processes amenable to easy field implementation. Second, with an integrated process, better quality control in processing can be achieved. For example, if the residual uranium in the soil is too high, the contaminated material can be recycled or the leachant reinjected. The same applies to water required for stripping the uranium from the soil. If the water is not acceptable for discharge, it can either be reused in the extraction process or recycled through the purification phase to reach the acceptable discharge criteria.

Finally, the innovative application of an ultrasonic field to both soil decontamination and purification of leachates provides an opportunity an efficient means of bulk contaminant removal in short contact (or reaction) times. In the ex-situ mode of soil treatment, the use of an ultrasonic field is expected to be suitable not only for uranium cleanup but to a broader range of heavy metals present in contaminated soils and sludges.

In the above context, the ex-situ and in-situ soil treatment technologies developed in this project are discussed in sections 5.6.1 and 5.6.2, respectively.

5.6.1 Ex-Situ Soil Treatment

(a) Technology Attributes

- In the soil treatment process, the bulk of the solid and liquid effluents produced is discharged after meeting the standards for discharge limits for the contaminants. In the case of Fernald soil, the recovered uranium concentrate can be reused in existing uranium milling operations. However, the recovered concentrate containing ^{90}Sr and ^{60}Co is more suitable for immobilization as secondary waste for disposal in a licensed low-level radioactive disposal facility.

- The ex-situ, integrated soil treatment process could be considered as a stand-alone technology with the addition of suitable material handling and solidification technologies on the front-end and the tail-end of the process. The key components of the proposed technology are sufficiently generic that they offer flexibility to adapt to a broad range of heavy metal contaminants present in soils.

- The exploitation of efficient contaminant removal schemes including ultrasonic leaching and precipitation are expected to be economically attractive for ex-situ applications. For this situation, the process is amenable to mobile operation which can be taken from site to site. This approach allows the capital investment to be spread over several applications by moving the process equipment from site to site. The volume of secondary waste generated can be low through efficient use of chemical additives required to remove mobile species from soil and solution matrices. All of these advantages may serve to reduce costs to remediate a contaminated site.

(b) Cost Analysis

Soil Treatment Based on the Proposed Process

In this section, preliminary capital and operating cost estimates for the proposed soil leaching and leachate treatment processes to decontaminate the Fernald Incinerator Area soil are summarized. A process flowsheet is designed and shown in Figure A.42, based on the results of bench-scale and pilot-scale tests in this study. A computer program was written in Lotus-123, release 4 for Windows to perform the material balance calculations for design and sizing of the process equipment, secondary waste estimation, and cost analysis. The assumptions used and the results of the material balance calculations for a 20 ton/h (tph) treatment plant are given in Table B.40.

The capital and operating cost estimates are based on a uranium soil treatment plant which has a throughput capacity of 20 tph (1,070 gpm for soil leachate treatment process) and a 87 percent plant on-line time (total operating time is 7,200 h/y). The plant will treat nearly 144, 000 tons of contaminated soil per year. The plant life is assumed to be 5 years for depreciation calculations. The costs reported are in 1995 values, and the accuracy of the cost analysis is expected to be within ±30%. The preliminary cost estimates for the soil leaching and leachate treatment processes are summarized in Tables B.41 and B.42, respectively.

The following assumptions were made regarding the contaminated soil influent and operating conditions. The feed soil composition is summarized in Table B.5. It contains about 500 mg/kg of uranium. The soil leaching is carried out at a liquid to solid ratio of 10. Chemical additions include 0.025 mol/L sulphuric acid and 0.03 g/g potassium permanganate for soil leaching step, and 0.012 kg/L sodium hydroxide and 5 mL/L 30% hydrogen peroxide for leachate treatment step. Each process involves chemical addition and conditioning in an ultrasonic field, followed by pre-coat filtration. The treated soil is washed by water to remove surface contaminants and neutralized the soil pH. The target uranium level in the treated soil is 52 mg/kg (35 pCi/g). The treated water pH is around 10.5 and is neutralized with carbon dioxide prior to discharge. The uranium concentration in the treated water is targeted for the drinking water limit or within one order of magnitude of the drinking water limit. The secondary waste produced from the process is transferred off-site for re-use. Details of contaminant removal efficiencies are given in Table B.40 (footnotes (3) and (4)).

The direct capital cost includes costs of materials and labour involved in the installation of the complete facility. This includes costs of equipment, equipment installation, instrumentation and control, piping and valves, electrical etc. A "percentage of delivered equipment cost" method [Peters and Timmerhaus 1980] was used to estimate plant capital cost. The percentages used for cost estimation are dependent on the type of process involved, design complexity, required materials of construction, plant location, and past experience.

The equipment costs were extracted from the data compilation of Gumerman et. al. [1979a; 1979b; and 1986], Hansen et. al. [1979], Mular [1978], and Peters and Timmerhaus [1980]. Selected equipment costs were also obtained directly from the vendors. Cost data were updated to 1995 values using the Marshall and Swift equipment cost indices as applicable.

The primary equipment for the direct capital cost estimation of soil leaching plant included belt conveyors, ball mill, screening system, soil feeding system, water heating system, sulphuric acid addition system, oxidizing agent addition system, slurry pumps, ultrasonic mixing system, filter-aid addition system and filtration system.

The major equipment in the leachate treatment process included conditioning tanks, transfer pumps, pH chemical addition system, oxidizing agent addition system, ultrasonic mixing system, filter-aid addition system, filtration system, and neutralization system. It was assumed that 80% of the design capacities of various equipment would be used in normal operation. Excepting for transfer pumps, no redundancy was allowed for other equipment.

The site related cost such as building, yard improvement and the facility start-up related items including engineering and project management costs were also included in the fixed capital cost estimation. The preliminary estimation of the capital costs for the soil leaching plant and the leachate treatment plant are $10,885,500 and $8,329,000, respectively.

The operating cost includes the labour and material costs involved in the operation of the plant. They included labour costs for operation and maintenance, supplies (chemicals and spare parts), consumable (electricity, water and compressed air), analytical services, depreciation, taxes, insurance, and plant overhead. Fixed charges for permit and regulatory, and demobilization were included in the operating cost estimation to account the expenditures of these two activities up-front and after the soil decontamination.

Bulk price quotes for chemicals were obtained from the suppliers. A shipment cost of $60/ton was included in the total chemical cost. The electricity cost of $0.06/kW.h was used. Process water cost was estimated to be $2/150 gal. An average labour cost of $32/h was employed for technician, supervisor, operator, maintenance worker and construction worker.

A straight-line method was used to estimate the equipment depreciation cost. The local taxes and insurance were assumed to be 2 % of the fixed capital cost. The plant overhead cost and adminstration cost were 50% and 15% of the labour and maintenance costs, respectively.

The effluent disposal cost includes costs for on-site storage, transportation, and disposal of effluent. The effluents from the process include treated soil and water. The treated soil is assumed to be suitable as backfill on-site from where the original contaminated soil had been excavated for treatment. The treated water may be suitable for discharge via sewer treatment plant, or may be treated further to reduce the total dissolved solids and sulphate levels, prior to unrestricted discharge. In the preset cost estimate, no additional effluent disposal cost was included for the post-treatment of the uranium-depleted effluent.

The secondary waste management cost consists of costs for storage, transportation and disposal through reuse at an existing uranium milling operation. The wet cake containing uranium is the only secondary waste generated from the process, and it is shipped off-site (about 1,000 km) for reuse. A transportation cost of \$150/m^3 and a container cost of \$18/m^3 were used for the handling and management of the secondary waste.

The financial analysis showed that the capital cost of the soil leaching plant is \$10,885,500, and the annual operating cost is \$26,352,700. The unit cost for the soil leaching process is about \$180/ton. The capital and annual operating costs for the soil leachate treatment plant with throughput capacity of 1070 gpm are estimated to be \$8,329,000 and \$21,785,400, respectively. The cost of treating 1,000 gallons of soil leachate is about \$47. When the operating cost of the two treatment plants are combined, the unit soil treatment cost using the proposed treatment flowsheet totals \$334/ton.

Direct Disposal of Contaminated Soil

In a recent evaluation [STF, 1994] for moderately uranium contaminated soil in Canada, a preliminary assessment of different technologies were made. In many respects these soils are similar to the Fernald soils with uranium being the only radioactive element present. The uranium isotopic analysis show essentially natural uranium characteristics [see for example, LANL, 1994]. They included: 1) fixation or stabilization; 2) soil washing (only physical separation); 3) in-situ stabilization/solidification; 4) cap and cover; and 5) direct disposal. For this evaluation, the cost data were taken from Environment Canada data base [SEDTEC, 1993]. Among the different options considered in this study, it appears direct disposal may be considered as a potential option for managing the uranium soils similar to the Fernald soil. By this option, the contaminant in the Fernald soil may be considered as a `naturally occurring radioactive material' (NORM). As a result, the soil can be disposed in a site such as the one operated by Envirocare of Utah, Inc. at Clive, Utah. It is also assumed in this option that the waste soil can be placed in bulk without containers. The dry waste can be encapsulated using clayey binders and capped with a rushed rock intrusion barrier (normally practiced by Envirocare for NORM wastes from locations across the U.S.). Upon consideration of the costs for waste transportation, adjustment for ISO container requirements for transportation, disposal, and an allowance for costs associated with environmental assessment and public review [STF, 1994], a preliminary overall cost of managing the soil would be expected to be in the order of \$300 per ton of soil.

On the basis of the assumptions used and likely errors in the cost estimate of ±30%, it appears that the overall soil treatment cost and the overall cost for direct disposal of the soil without treatment can be similar. Evidently, the main difference is that the treatment of the uranium soil and reuse of the extracted uranium is an environmentally conducive and sustainable option without long-term issues. The direct disposal, on the contrary, may not have the public perception of a responsible action. In any case, a detailed engineering design and cost calculations are essential to establish the economics associated with these options.

5.6.2 In-Situ Soil Treatment

(a) Technology Attributes

The integrated in-situ and ex-situ soil treatments differ only with respect to the soil leaching portion of the process. The soil leachate treatment portion of the in-situ method is identical to the ex-situ treatment. The in-situ soil leaching involves leachant injection through wells into subsurface soil. The leachant may consist of the basic leachant chemical (e.g., dilute mineral acid) and other agents such as oxidising or reducing chemicals. Because of the large amount of soil to be decontaminated, the fluid injection rate would vary and the rate would be controlled by the permeability and hydraulic conductivity of the soil.

The mechanism of contaminant removal is similar to solute transport in fixed-bed ion-exchange columns. The leachate produced after extraction of the contaminants from the soil then migrates to a collection or production well. The collected leachate is treated by above ground facility, similar to ex-situ leachate treatment. The soil leaching portion of the in-situ treatment has several common features with chemical and microbial enhanced oil recovery [Borchardt, 1995]. One important consideration is that the chemicals used in soil leaching should not cause additional environmental damage.

The in-situ soil treatment is best suited for large contaminated subsurface areas consisting of unsaturated and saturated soils. The common problem is that the spatial distribution of the contaminants within the soil may not be uniform, leading to non-uniform distribution of injected leachant and finally reduces the contaminant removal efficiency. In certain instances, the injected leachant may bypass pockets of contaminants and also high permeability zones can be easily plugged. Positioning of the injection and production wells within critical spacing is expected to provide a more reliable and uniform contaminant removal performance.

In terms of target clean up goal, in-situ soil leaching still faces some problems, primarily due to uncertainties associated with the uniformity of contaminant distribution in the treated soil. In the absence of reliable in-line analytical instruments suitable for spatial imaging of the contaminant profiles underground, costly borehole soil sampling would be required.

The in-situ soil leaching process is capable of removing in one step both radionuclides and toxic heavy metals. Where in-situ remediation is possible, the soil does not have to be moved or handled, which reduces hazards associated with inhalation of fine dust particles to which the heavy metals or radionuclides may be attached. Removal of contaminants from spreading plumes and from the source of the contamination will substantially reduce or eliminate future risks to the health of critical individuals.

Because of the lack of reliable cost data, cost estimates for the in-situ soil leaching was not carried out in the present study. It is anticipated, however, that the soil-leaching portion of an integrated in-situ plant, in addition to reducing worker and public risks, should be less labour intensive and hence potentially cheaper at least for sandy soils, such as the AECL Chalk River soil, contaminated with easily removable radionuclides and other heavy metals.

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

6.1.1 Bench-scale Ex-situ Soil and Leachate Treatment

(a) Flotation of Contaminated Soils as a Preconcentration Step

- Among the different chelating agents tested as the flotation collector for uranium in the Fernald Incinerator Area soil, the use of cupferron produced some promising results: 42 wt% of the original soil was floated, containing 72% of the uranium originally present in the soil, while the residual uranium concentration in the non-float ("clean soil") contained about 300 mg U/kg. These results were below the desired target of 93% uranium recovery in 20% of the mass floated. Selective flotation was not possible since an appreciable amount of uranium was associated with the fines and the clay fractions of the soil.

- For the Chalk River Chemical Pit soil, preconcentration of the soil by selective flotation of trace amounts of radionuclides (^{90}Sr, ^{60}Co, U, ^{137}Cs) was not found to be a viable method. Reasons for the failure to achieve selective flotation include: near uniform distribution of the contaminants in the soil matrix; and, the presence of extremely low concentrations of the contaminants.

- Since a detailed examination of the flotation process, especially the application of relatively unconventional selective flotation reagents was beyond the project scope, further refinement of the flotation technique was not pursued.

(b) Soil Treatment by Ultrasonically-Aided Chemical Leaching

- The removal of contaminants from both the Fernald Incinerator Area and the Chalk River Chemical Pit soils was achieved efficiently using chemical leaching at short soil-leachant contact times (1 to 3 minutes) in the presence of an ultrasonic field at a fixed frequency of 20 kHz. Ultrasonic energy input of 30 kJ/L or less was found to be adequate to achieve high contaminant removal efficiencies.

- For low-energy inputs (corresponding to three minute leaching per stage), ultrasonically-aided leaching was superior to leaching with mechanical agitation.

- A comparison of ultrasonically-aided soil leaching results under batch and recirculation modes of testing suggest that mixing input energy/volume may have to be decoupled into "power intensity" and "contact time" parameters to establish scale-up criteria.

- For Fernald soil, there were no specific requirements for additional grinding of the soil prior to leaching. However, prescreening of the feed soil to remove the gravel portion was necessary. For Chalk River Chemical Pit soil, the need for additional grinding of the feed soil (average particle size: 185 μm) prior to leaching was not clearly established as the majority of tests were performed using soil samples of 75 μm average particle size. The adsorbed-state of the radionuclides in the soil suggests that grinding may not be necessary.

- Among the three groups of leachants (chelating, alkaline and acidic) studied, mineral acid leaching was found to be the most effective to remove the radionuclides from the Fernald Incinerator Area and the Chalk River Chemical Pit soils to meet the target value of 35 pCi/g of treated soil.

- To ensure and to meet the target level of uranium in the treated soil, a two-stage leaching of the Fernald soil with 0.5 mol/L sulphuric acid with potassium permanganate (0.003 to 0.03 g/g of soil) at 50 °C was required. The uranium concentration in the treated soil was 30 % higher and 40 % lower than the target in single-stage and in two-stage leaching, respectively. It is possible that an optimized single-stage leaching flowsheet may be sufficient to meet the target.

- The use of 0.1 mol/L sulphuric acid with air or potassium permanganate in two-stage leaching at 65 °C produced a treated soil with a uranium concentration 1.75 times higher than the target value whereas a single-stage leaching produced twice the target value. Sulphuric acid at higher concentrations in combination with an oxidizing agent (air or potassium permanganate) was effective for the removal of uranium from Fernald soil to the established target value of 35 pCi/g for treated soil.

- By comparison, the equimolar concentrations of sodium carbonate and sodium bicarbonate at 0.1 mol/L and 0.3 mol/L, and a leach temperature of 50 °C brought uranium concentrations in the treated soil to within three to four times the target value. Mineral acid dissolved about 10% of the soil whereas the alkali dissolved about 4% in the leaching step.

- A two-stage hydrochloric acid leaching with 0.1 mol/L or 0.5 mol/L HCl, combined with a reducing agent sodium dithionite (0.002 g/g), at 50 °C was sufficient to remove ^{90}Sr, ^{60}Co and ^{137}Cs from Chalk River Chemical Pit soil to the target value of 35 pCi/g for treated soil. In the absence of sodium dithionite addition, the radionuclide level in the treated soil was about 50% greater than the target value. A single-stage hydrochloric acid leaching with sodium dithionite addition resulted in radionuclide concentrations in the treated soil of 1.3 to 1.8 times the target, whereas without sodium dithionite addition, the concentration was 1.6 times the target value. There was no advantage to increase the hydrochloric acid concentration to 0.5 mol/L.

- Reducing the concentration of mineral acid (H_2SO_4 or HCl) from 0.5 to 0.1 mol/L gave treated soil concentrations within a factor of 2 of the 35 pCi/g target.

- Bench-scale results suggest that two leaching stages was necessary to meet the target soil quality. However, the expectation was that on a continuous, engineering-scale plant a single-stage ultrasonically-aided soil leaching with adequate water-washing should be sufficient to meet the target quality for the treated soil.

- Within the analytical and experimental errors, the mixing energy-input parameter was found to be suitable to monitor the soil decontamination performance, provided the redox chemistry conditions were kept constant.

- Generally, increasing the soil leaching temperature to 60 to 65 °C and the leaching time to more than three minutes may reduce the leachant concentration requirement.

(c) Ultrasonically-Aided Soil-Leachate Treatment

- Bench-scale results showed that acidic leachates can be treated effectively through ultrasonically-aided precipitation/sorption at room temperature (25 to 30 °C), involving low energy-input values in the range of 30 to 40 kJ/L of solution, or less. Contact times of less than 1 min (in the presence of a 20 kHz ultrasonic field) should be sufficient to complete the precipitation/sorption of contaminants and other metals.

- The removal of uranium by precipitation/sorption from leachates containing alkali and chelating agents was not simple and needed further investigation.

- The need for a polishing step was identified to control the total dissolved solids, divalent anions (e.g., SO_4^{2-}) and monovalent anions (Cl^-) present in the treated water, before discharge or reuse.

- For Fernald Incinerator Area soil, uranium from acidic sulphate leachate was removed readily to the desired target value by the addition of lime, H_2O_2 and a ferric salt at a solution pH of 10. The total dissolved solids were reduced to about 10% of the initial value. A single-stage, ultrasonically-aided process was found to remove uranium easily to meet the MPC of 0.29 mg U/L stipulated by ICRP [1977].

- Reduction of uranium to 0.06 mg/L or less (USEPA Drinking Water Limit) may require two leachate-treatment stages. The results also showed that a relatively high secondary waste solid mass (about 30 g dry solids/liter of leachate treated) was produced with lime addition. The use of $Mg(OH)_2$ or NaOH instead of lime reduced the amount of secondary waste as much as 5-fold. This aspect will be a key factor to evaluate options in the pilot-scale test program for secondary-waste disposal or reuse.

- Treatment of hydrochloric acid leachate generated from Chalk River soil leaching with the addition of lime and soda or lime, soda and a natural zeolite in the presence of a 20 kHz ultrasonic field removed ^{90}Sr and ^{60}Co effectively in a contact time of about 1 minute to a level that meets the Maximum Allowable Concentration for these radionuclides ($[^{90}Sr] = 270$ pCi/L and $[^{60}Co] = 2700$ pCi/L), as recommended by the ICRP [1977]. The ICRP drinking water guideline was used in the bench-scale tests because the sample detection limit for the bench-scale tests was limited to 108 pCi ^{90}Sr/L, 540 to 810 pCi ^{60}Co/L and 240 to 540 pCi ^{137}Cs/L as a result of the availability of only small sample volumes for radiochemical analysis.

- Uranium removal from the Chemical Pit soil leachate met the USEPA [1990] drinking water guideline of 0.06 mg/L.

6.1.2 Bench-scale Soil Column Study

- Leaching of the Chemical Pit soil (average concentrations of 217 pCi ^{90}Sr/g and 14.6 pCi ^{60}Co/g) in 400 g soil columns with 0.1 mol/L HCl in the presence and absence of 770 mg/L sodium dithionite as reducing agent at 5 °C was performed to simulate the field test conditions.

- Increasing the soil column leaching temperature to 25 °C gave no significant improvement to ^{90}Sr removal efficiency, although iron present in the soil was released rapidly to a concentration of about 350 mg/L in the column leachate after 5 pore volumes had passed through the column. By comparison, the concentration of iron in the leachate at 5 °C was 120 mg/L. The higher iron release at 25 °C was attributed to the temperature effect on the kinetics of iron dissolution in acidic conditions.

- The addition of two pore volumes of sodium dithionite solution at 770 mg/L, prior to 0.1 mol/L HCl leaching, resulted in a large release of iron, peaking at 1700 mg/L in the leachate after a passage of 2.5 pore volumes of dithionite solution. For the same conditions, the ^{90}Sr also peaked at a concentration of 1500 pCi/L. The results indicated that sodium dithionite leaching alone was sufficient to remove the contaminants to meet the target level of 35 pCi (^{90}Sr + ^{60}Co)/g of treated soil.

- Soil column leaching with 0.1 mol/L HCl at 2.5 pore volume leachant addition removed 75 to 80 % of the ^{90}Sr and almost all of the ^{60}Co activity.

- Soil column leaching results compared well with the bench-scale ex-situ soil leaching results in showing that the use of dilute hydrochloric acid with and without the addition of sodium dithionite as reducing agent were effective in removing ^{90}Sr from the contaminated aquifer sand. Soils used for the bench-scale ex-situ leaching tests had average concentrations of radiostrontium and cobalt about five times higher than that of the soil used in the soil column experiments.

- A leachant volume of 3 to 4 pore volumes was found to be adequate to leaching essentially all radiostrontium and cobalt from the soil. The removal efficiencies corresponded to a treated soil concentration of about 8 pCi/g (or about 0.3 Bq/g) of combined radiostrontium and cobalt, which is about a factor of 4 lower than the target residual activity in the treated soil of 35 pCi/g (1.3 Bq/g).

6.1.3 In-situ Soil Treatment Field Study

- In spite of the premature stoppage of leachant addition, fall temperatures (5 to 10 °C) and relatively high dispersivities of the soil (0.4 m), primarily due to test cell geometry, the in-situ soil leaching test removed over 90% of the ^{90}Sr contained in the test cell. The result was achieved by the addition of 1.34 pore volumes of 0.005 mol/L sodium dithionite followed by 3.4 pore volumes of 0.1 mol/L HCl and then followed by 1.97 pore volumes of water. The average initial ^{90}Sr concentration in the soil was 258 pCi/g (9.56 Bq/g) and the average concentration in the treated soil was 27 pCi ^{90}Sr/g (1 Bq ^{90}Sr/g), which is below the target value of 35 pCi/g. Because of uncertainties in the ^{60}Co measurements, and the low initial concentration of ^{60}Co in the soil (1.3 pCi/g or 0.27 Bq/g), the removal efficiency data were not reliable.

- The field test was successful in demonstrating that ^{90}Sr contained in sandy soils such as the Chalk River soil can be mobilized easily using dilute mineral acid as a leachant.

- In large-scale in-situ treatment of sandy soils, the soil dispersivity values are expected to be much lower than observed in the present test cell, which would be favourable for increased ^{90}Sr removal efficiencies with reduced volumes of the leachant.

- The successful in-situ experiment demonstrated the utility and practicality of decontaminating aquifers containing ^{90}Sr. Radiostrontium is the most mobile of the relatively abundant fission products which have a half-life long enough to persist in appreciable amounts for a few hundred years, and it has a high radiotoxicity. Removing most of the ^{90}Sr from a number of aquifers at Chalk River Laboratories would qualify as final remediation, and the same is likely to be true at other sites.

6.1.4 Pilot-scale Ex-situ Soil and Leachate Treatment Study

Chalk River Soil Leaching

- In closed-loop recirculation mode soil leaching tests at high soil-leachant flow rates (~30 L/min) and long leach times (up to 60 min), the target value of less than 35 pCi (total beta and gamma) per gram of treated soil was achieved. Increasing the leach temperature by about 5 to 10 °C from the base temperature of 25 °C increased the contaminant removal efficiency. The effect of ultrasonic field in relation to circulation flow mixing in the removal of contaminants was not evident at long contact times.

- Once-through mode slurry leaching with a tubular ultrasonic liquid processor at low slurry flow rates (about 10 L/min), at 25°C, for extremely short leach times of about 4 to 5 seconds using 0.05 mol/L or 0.15 mol/L HCl produced treated soil concentrations which were about three times higher than the target value. The results obtained indicated that for this particular soil, the same level of contaminant removal could be achieved with flow mixing alone.

- The most surprising results from bench-scale and pilot-scale tests were that the soil leaching with water alone in the presence of an ultrasonic field at short contact times of 5 to 10 seconds was sufficient to remove about 40 to 48% of the ^{90}Sr originally present in the soil. This magnitude of removal was possible only in the presence of an ultrasonic field, suggesting that leachant additions even at low concentrations was sufficient to mask the ultrasonic effects on contaminant removal behaviour from this particular type of sandy soil.

- The soil leaching results showed that the contaminants, ^{90}Sr and gamma emitters including ^{60}Co, present in the Chalk River sandy soils used in the pilot-scale experiments were present in an easily removable form. This soil behaviour was found to be quite different from the higher radioactivity soil samples used in the bench-scale ex-situ soil leaching tests, where a two-stage leaching with a relatively concentrated acid solution (0.5 mol/L HCl), or a two-stage leach with 0.1 mol/L HCl at elevated temperature (50 to 60 °C) and an ultrasonic leach time of 60 to 180 seconds per stage was required to meet the target quality for the treated soil.

Fernald Soil Leaching

- Similar to Chalk River soil leaching results, the use of very long contact times (greater than about 80 min) at 40 °C, with or without an ultrasonic field combined with flow mixing due to slurry pumping, and 0.25 mol/L sulphuric acid and 0.03 g $KMnO_4$/g of soil was sufficient to decontaminate the Fernald Incinerator Area soil to less than 35 pCi U/g of soil.

- For the high slurry flow rate of 40 L/min employed, flow mixing combined with chemical leaching was found to be effective to reduce uranium levels for 1 second contact time, although the actual uranium concentration in the soil was about 20% greater than the results obtained from a superposition of a 30 kHz ultrasonic field over the flow mixing created by slurry pumping.

- The majority of uranium (75 to 80%) was removed at extremely short contact times (about one sec) by ultrasonically-aided chemical leaching of the soil.

- To meet the overall target quality for treated soil, the use of ultrasonic field may best be utilized in the initial reaction domain involving very low contact times (a few seconds), where the majority of the contaminants present originally in the soil is removed in an accelerated fashion.

- Soil leaching with sodium bicarbonate/carbonate solutions, in the presence or absence of ultrasonic mixing, alone was not sufficient to reduce the uranium level to meet the target. Similar to sulphuric acid leaching, the addition of an oxidizing agent such as $KMnO_4$ would be essential to provide the desired uranium removal efficiency. Although this aspect of the work was not examined in the present study, a satisfactory process chemistry in concert with ultrasonic mixing is anticipated to provide a process that would produce low volumes of secondary waste. It is also expected that the concentration of the alkaline leachant required would be reduced favourably. An important aspect of the alkaline leaching is that the soil slurry was very difficult to dewater.

Soil Leachate Treatment

- Soil leachate treatment to remove primary contaminants (uranium from Fernald soil leachate and ^{90}Sr from Chalk River soil leachate) was achieved effectively using a precipitation process in the presence of flow and ultrasonic mixing at room temperature.

- In the presence of a low frequency (30 kHz) and low power (about 700 W) ultrasonic field, a continuous treatment of soil leachate through precipitation at room temperature (20 to 25 °C) using a flow rate of about 5 L/min and low contact times (a few seconds) was sufficient to remove over 99% of the contaminants and other metals.

- To minimize the secondary waste volume generated by the treatment process, it was necessary to use precipitation chemicals such as sodium hydroxide, which resulted in relatively high total dissolved solids (TDS) in the effluent. Specifically, for Fernald soil leachate, sulphate ion was the main contributor to the TDS. To meet a suitable discharge criterion, this effluent would require further treatment. One option would be to discharge it to biological activated sludge sewage treatment plant, where the excess sulphate can be removed, or add an existing bacterial sulphate reduction technology.

6.1.5 Waste-Form Evaluation for Secondary Waste Produced from Chalk River Soil Leachate Treatment

- The compressive strength and leachability indices of contaminants concerned for the cemented waste form with a waste to cement ratio of 1 to 1 by weight exceed the performance criteria specified by USNRC. There appears to be some room to increase the amount of waste to cement ratio to achieve reduced volume of the final waste for storage/disposal.

Overall

- The cavitational energy produced by low frequency ultrasonic fields is an additional driving force which can be utilized synergistically in conjunction with chemical reagents and bulk flow mixing to achieve rapid removal of the majority of contaminants in extremely low contact times from soil and solution matrices.

- The removal of contaminants at low contact times together with micromixing characteristics of ultrasonic irradiation has many perceived beneficial effects. They include: a) compact reaction systems; b) smoothens out soil heterogeneity; c) primary chemical effects (oxidation, reduction and solubility) are exploited in short times using less severe chemicals and conditions; and d) more advantageous for decontamination of refractory soils.

- The ultrasonically-aided chemical leaching of soils is best suited for soils such as the Fernald Incinerator Area soil primarily because the soil consists of clayey fine particles and refractory contaminants. Excessive levels of flow mixing, high leachant concentrations, high temperatures and long contact times can mask the ultrasonic effects.

- The use of ultrasonically-aided contaminant removal offers, in addition, a unique means of carrying out treatability studies, pilot-scale technology demonstration at different sites using easily transportable equipment.

- Considering the total equipment cost of a pilot- or engineering scale soil treatment plant, the cost of ultrasonic equipment, based on available retail price, is about 5 to 7.5% of the total equipment cost. It is expected that this cost would reduce significantly as the demand for the ultrasonic systems increases.

- On the basis of the assumptions used and likely errors in the cost estimate of ±30%, it appears that the overall cost of \$334 per short ton of soil treated by our integrated, ex-situ soil and leachate treatment and the overall cost for direct disposal of the soil without treatment in the Envirocare's Utah facility can be similar. Evidently, the main difference is that the treatment of the uranium soil and reuse of the extracted uranium is an environmentally conducive and sustainable option without long-term issues. The direct disposal, on the contrary, may not have the public perception of a responsible action. In any case, a detailed engineering design and cost calculations are essential to establish the economics associated with these options.

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APPENDIX A

FIGURES DISPLAYING SELECTED EXPERIMENTAL AND ANALYSIS RESULTS

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

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LIST OF FIGURES (continued)

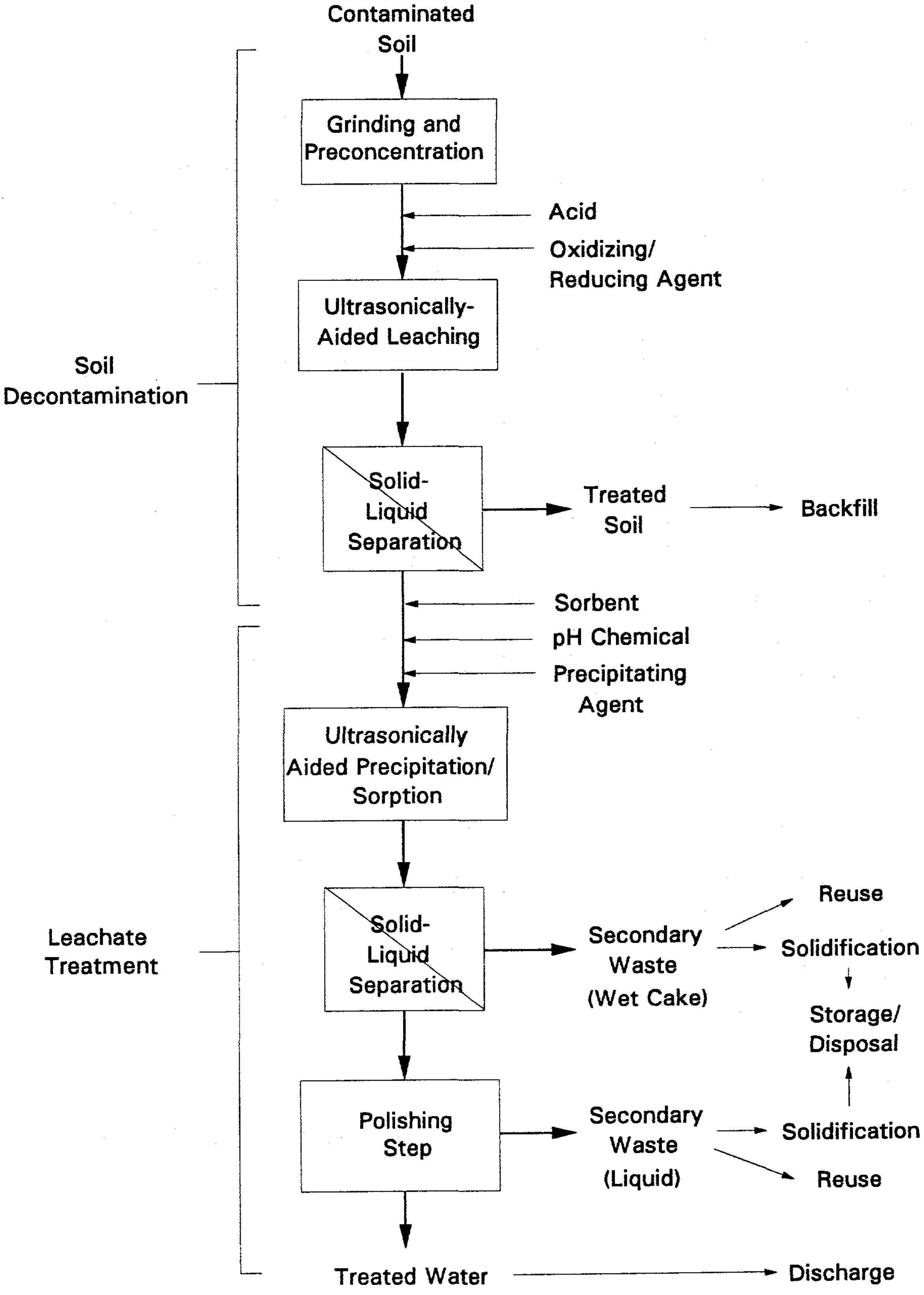


Figure A.1: Flow Diagram for Ex-Situ Soil Decontamination and Soil-Leachate Treatment

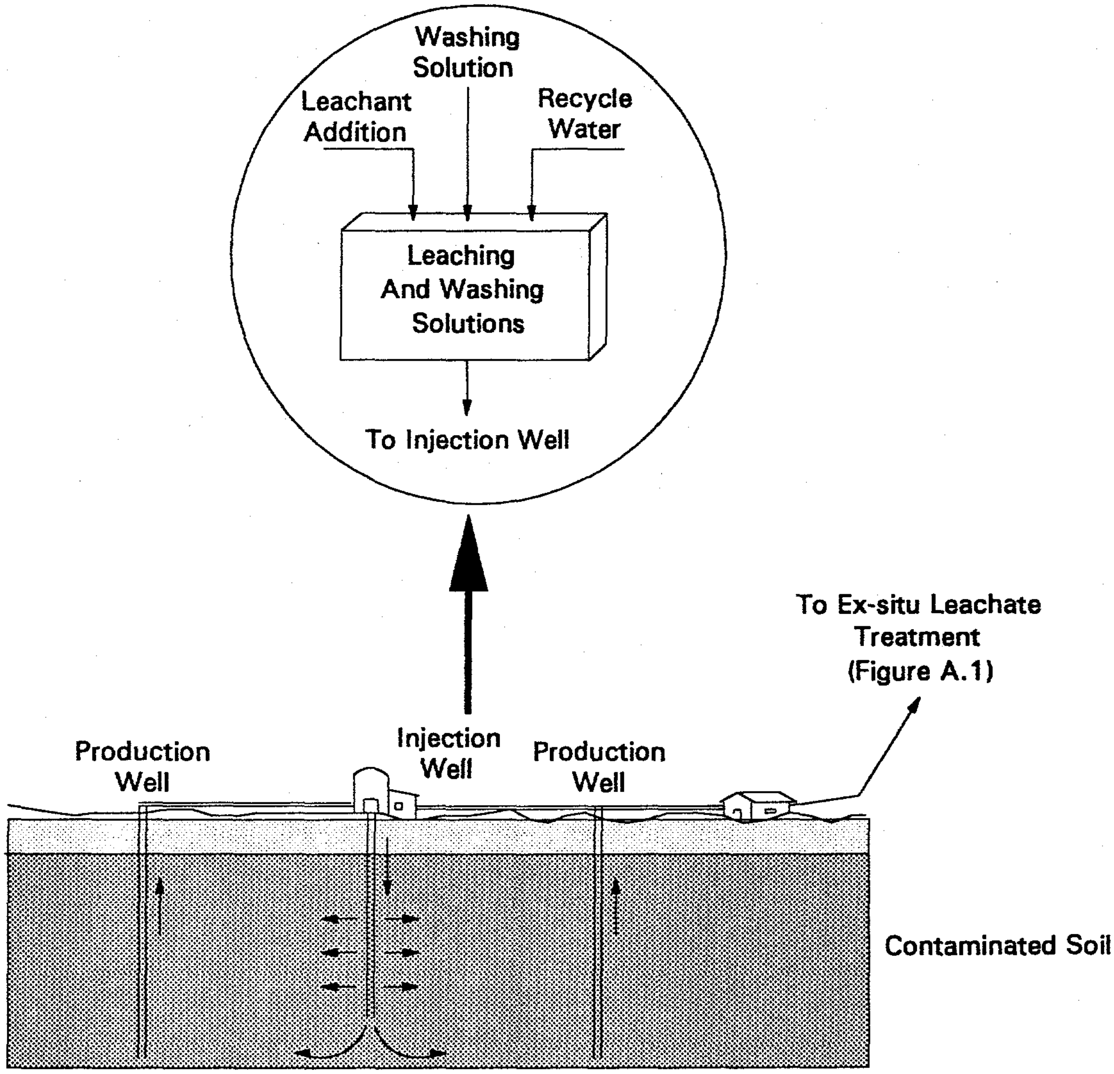
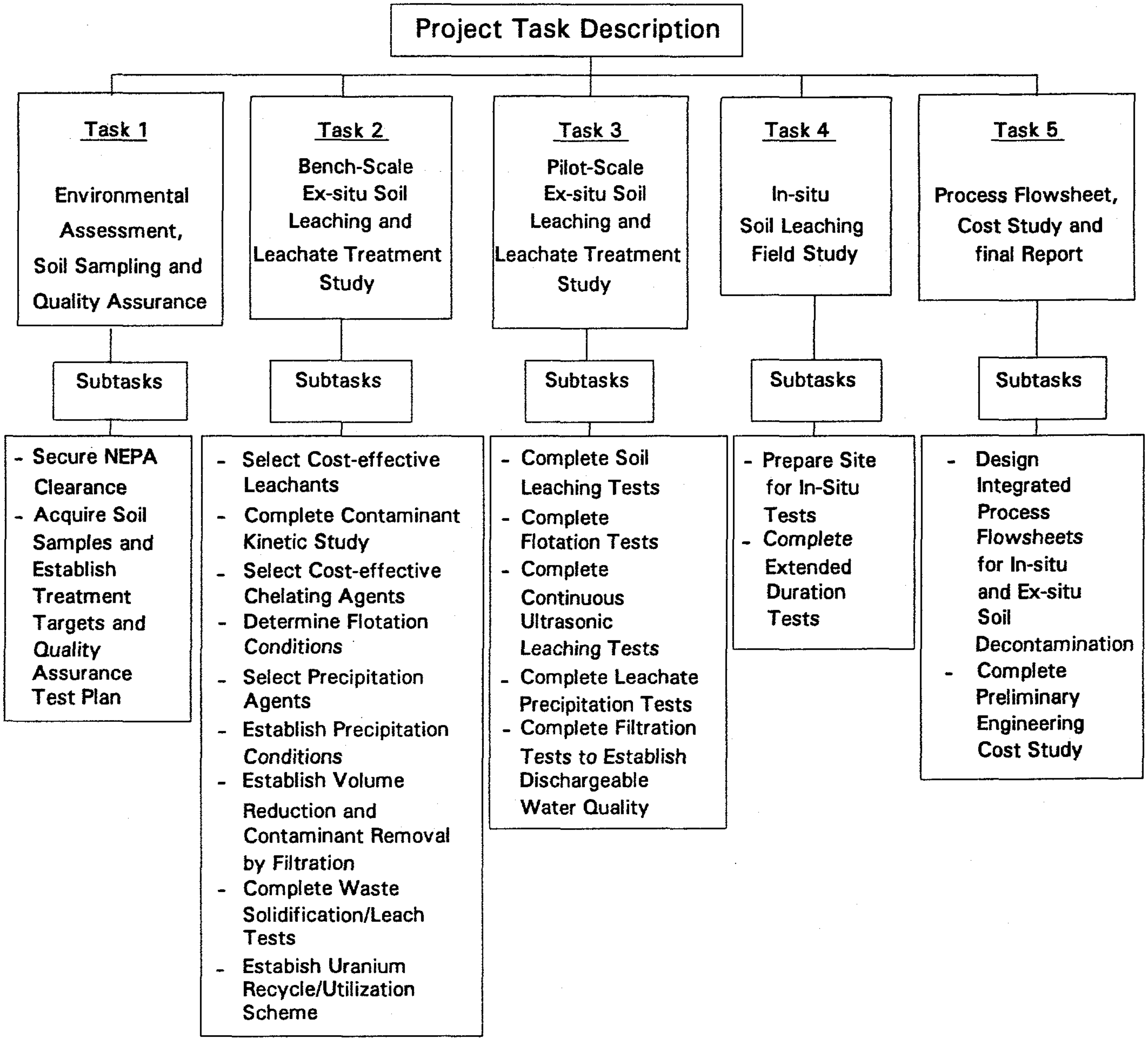


Figure A.2: The Proposed Process Scheme for In-Situ Treatment of Contaminated Soils



Project Task Description

Task 1

Environmental Assessment, Soil Sampling and Quality Assurance

Subtasks

- Secure NEPA Clearance
- Acquire Soil Samples and Establish Treatment Targets and Quality Assurance Test Plan

Task 2

Bench-Scale Ex-situ Soil Leaching and Leachate Treatment Study

Subtasks

- Select Cost-effective Leachants
- Complete Contaminant Kinetic Study
- Select Cost-effective Chelating Agents
- Determine Flotation Conditions
- Select Precipitation Agents
- Establish Precipitation Conditions
- Establish Volume Reduction and Contaminant Removal by Filtration
- Complete Waste Solidification/Leach Tests
- Estabish Uranium Recycle/Utilization Scheme

Task 3

Pilot-Scale Ex-situ Soil Leaching and Leachate Treatment Study

Subtasks

- Complete Soil Leaching Tests
- Complete Flotation Tests
- Complete Continuous Ultrasonic Leaching Tests
- Complete Leachate Precipitation Tests
- Complete Filtration Tests to Establish Dischargeable Water Quality

Task 4

In-situ Soil Leaching Field Study

Subtasks

- Prepare Site for In-Situ Tests
- Complete Extended Duration Tests

Task 5

Process Flowsheet, Cost Study and final Report

Subtasks

- Design Integrated Process Flowsheets for In-situ and Ex-situ Soil Decontamination
- Complete Preliminary Engineering Cost Study

Figure A.3: Overall Project Tasks

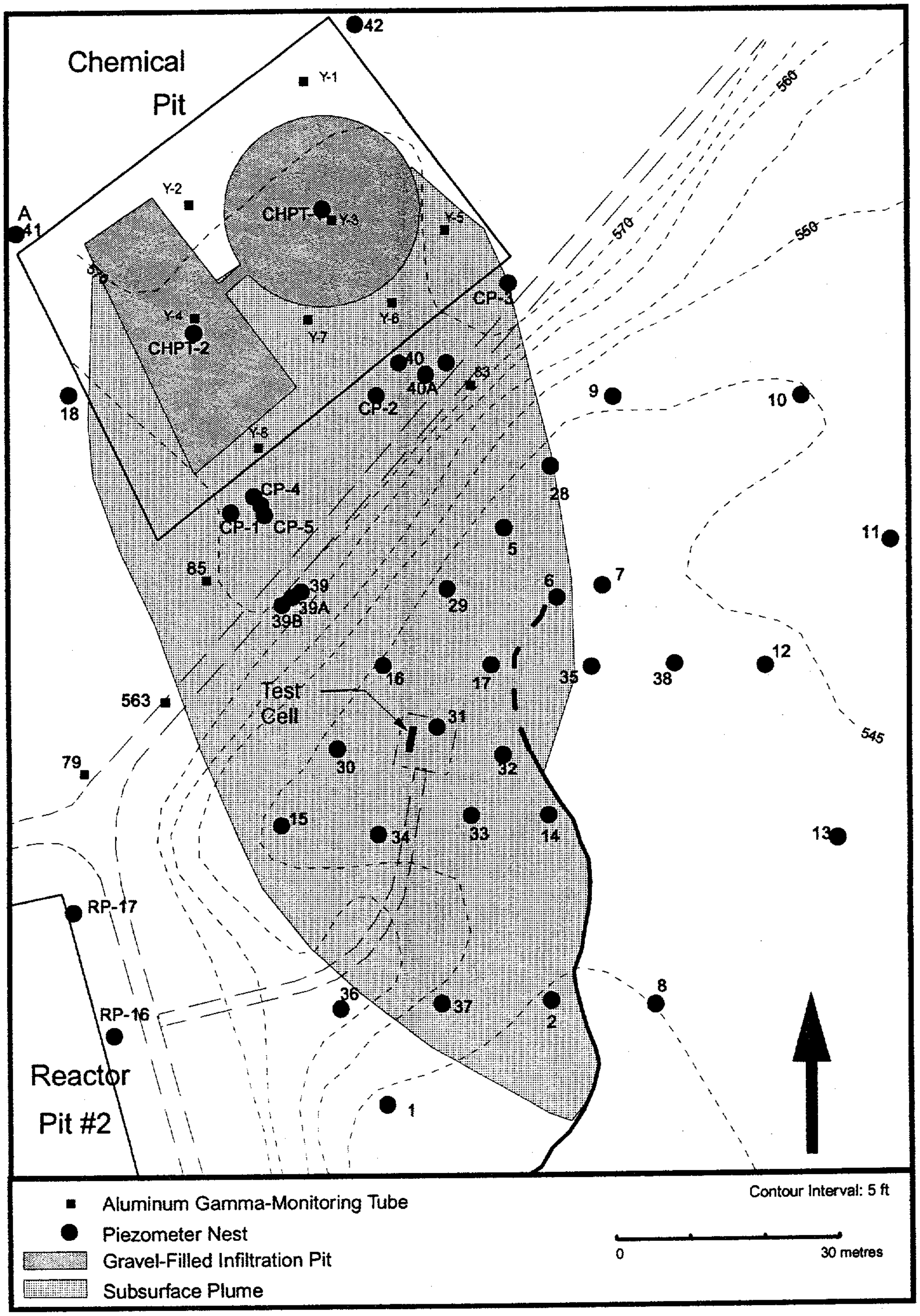


Figure A.4: Locations of the Chemical Pit and Associated Subsurface Monitors, the In-Situ Test Conducted for This Project, and the Plan View Extent of Groundwater Contamination Arising from the Pit

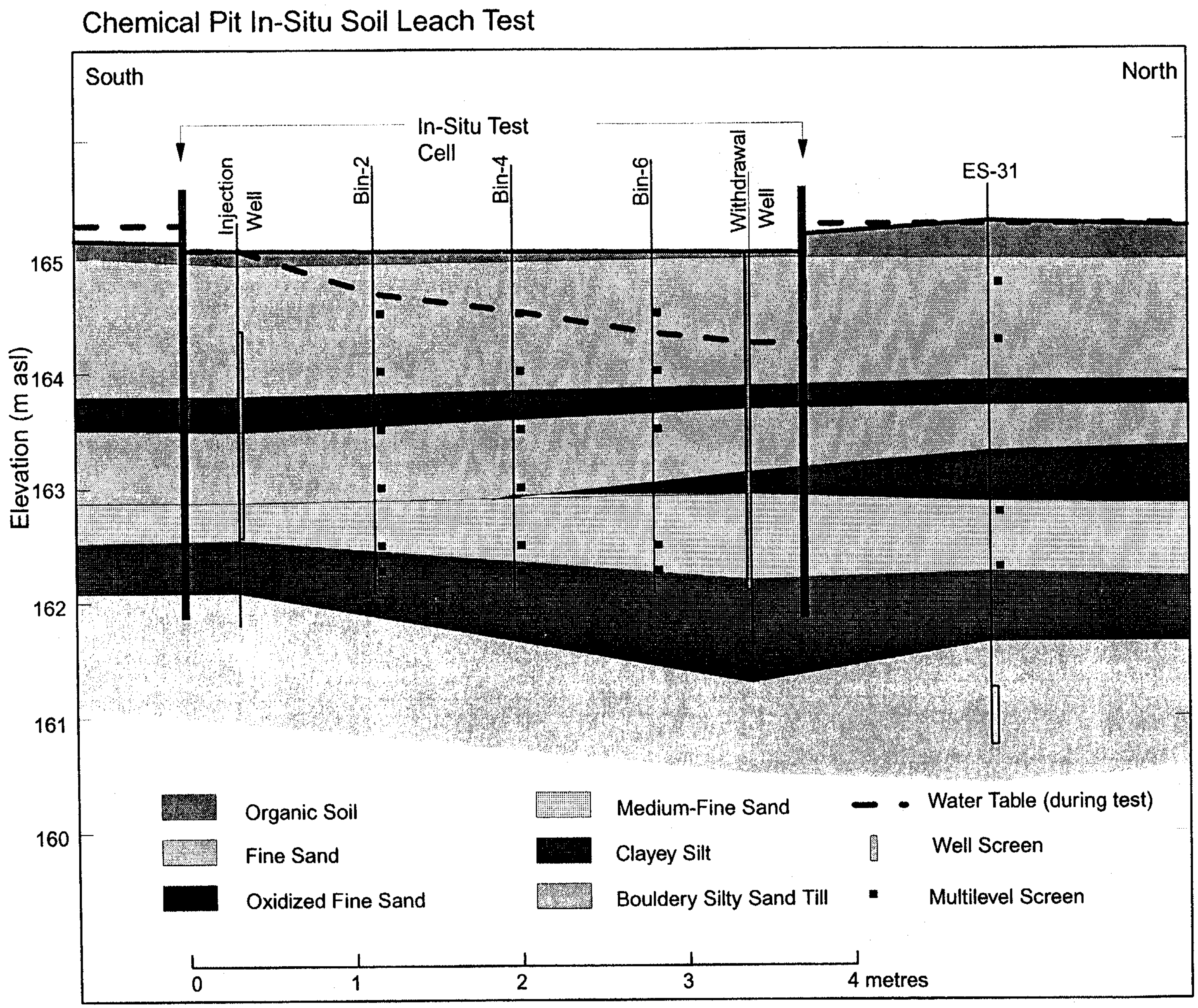


Figure A.5: Stratigraphy in the Chemical Pit Test Cell

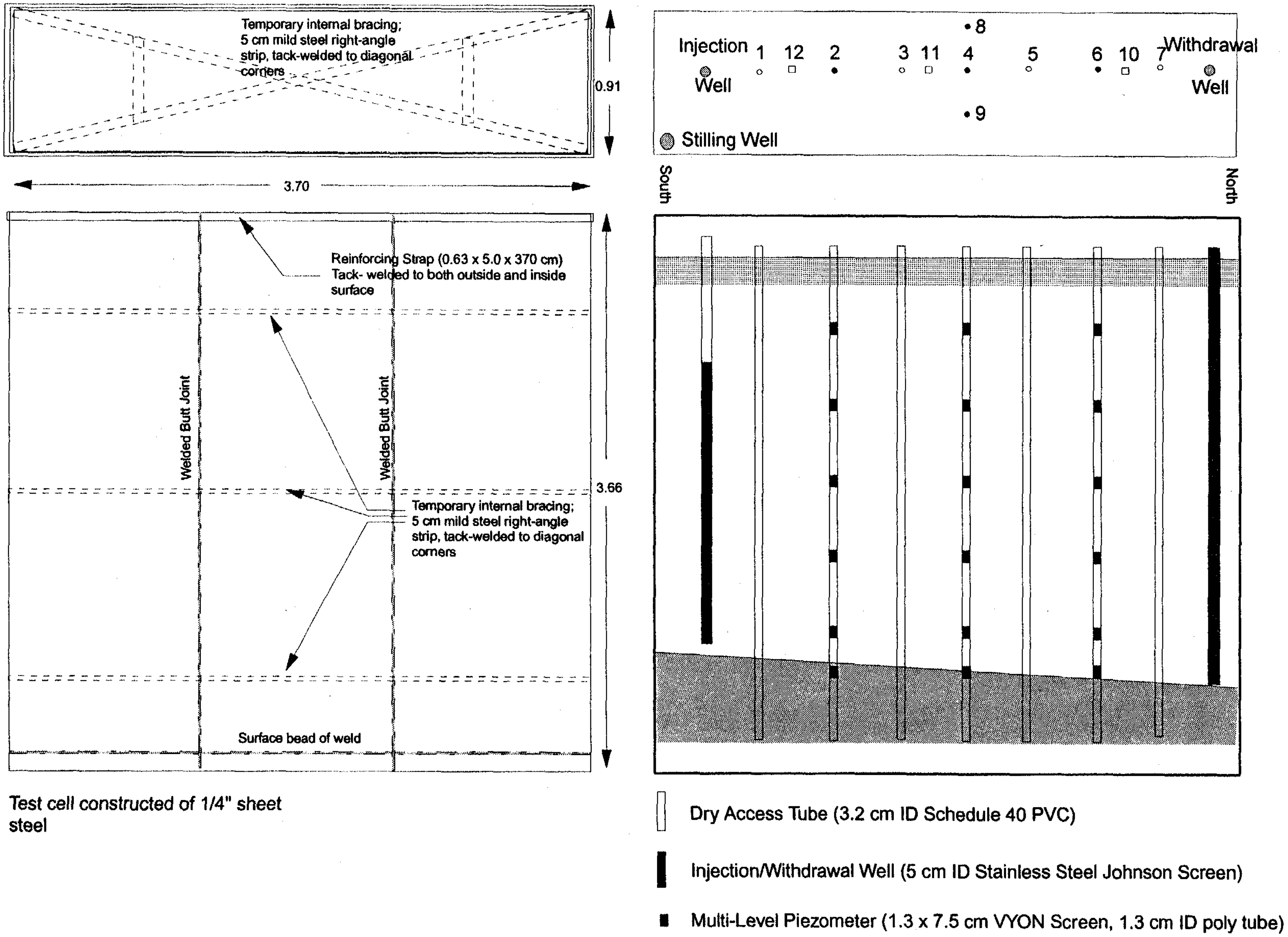


Figure A.6: Construction Details of the Test Cell, and the As-Installed Layout of Monitoring Equipment

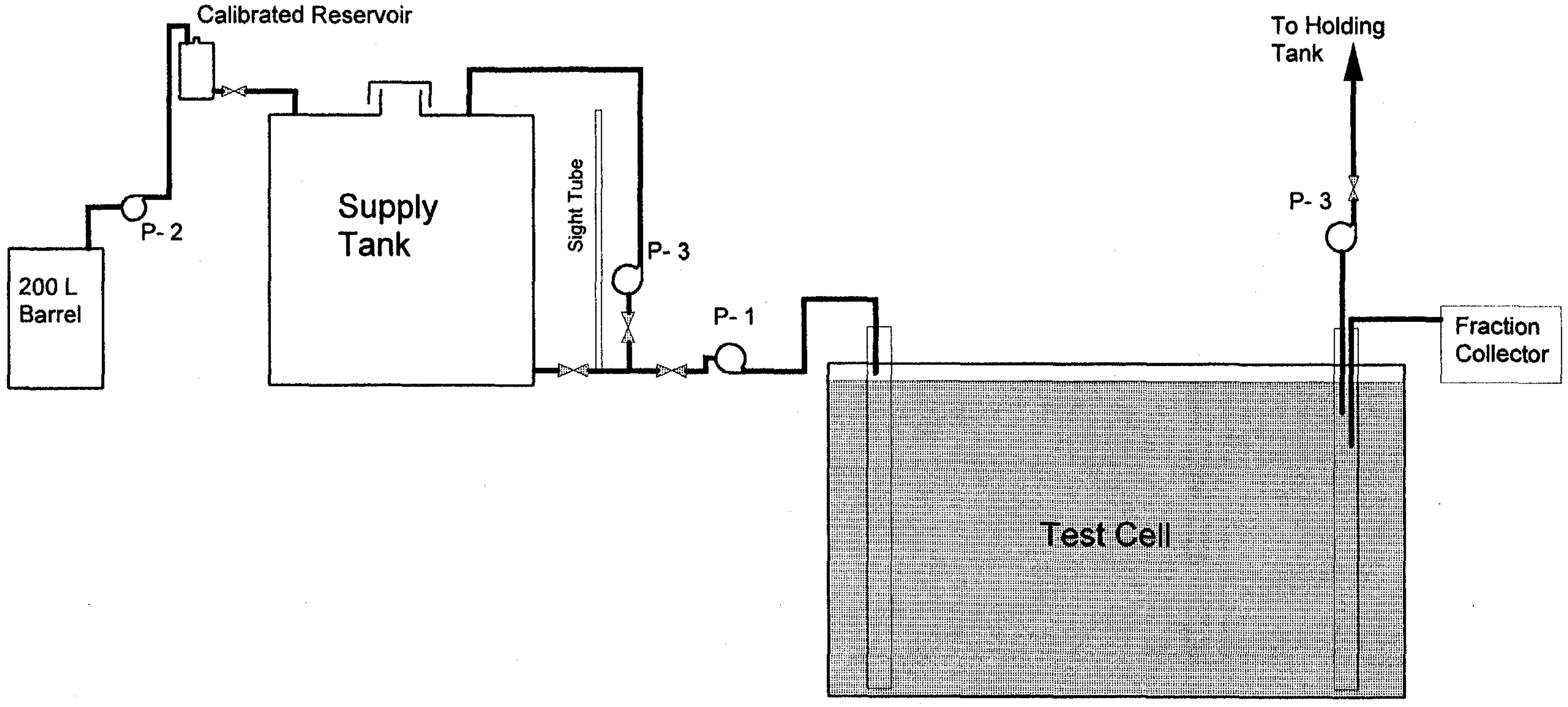


Figure A.7: Schematic of In-situ Soil Leaching Field Study Process

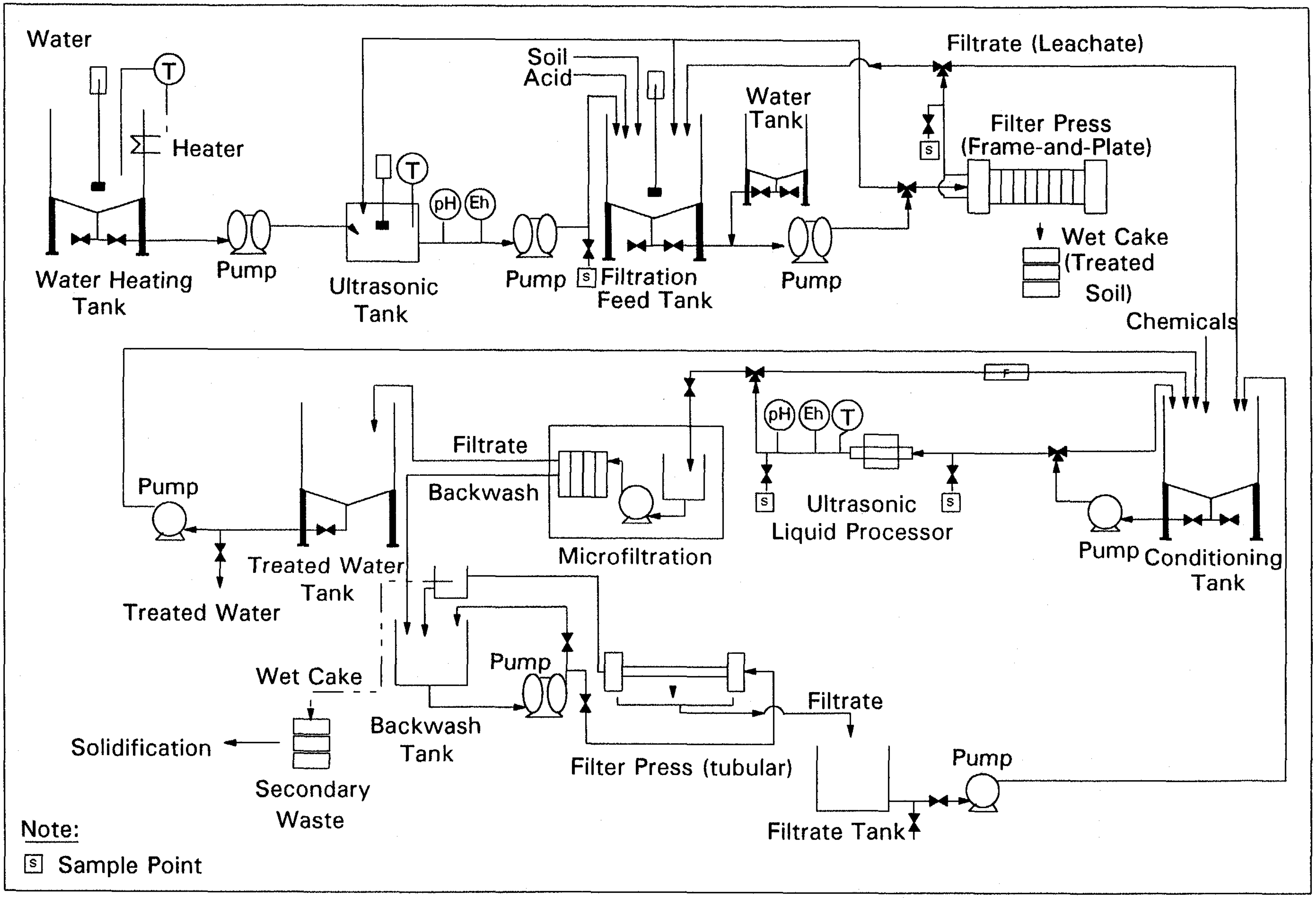


Figure A.8: Flowsheet for Pilot-Scale Soil Decontamination and Leachate Treatment Tests Using an Ultrasonic Tank for Soil Leaching

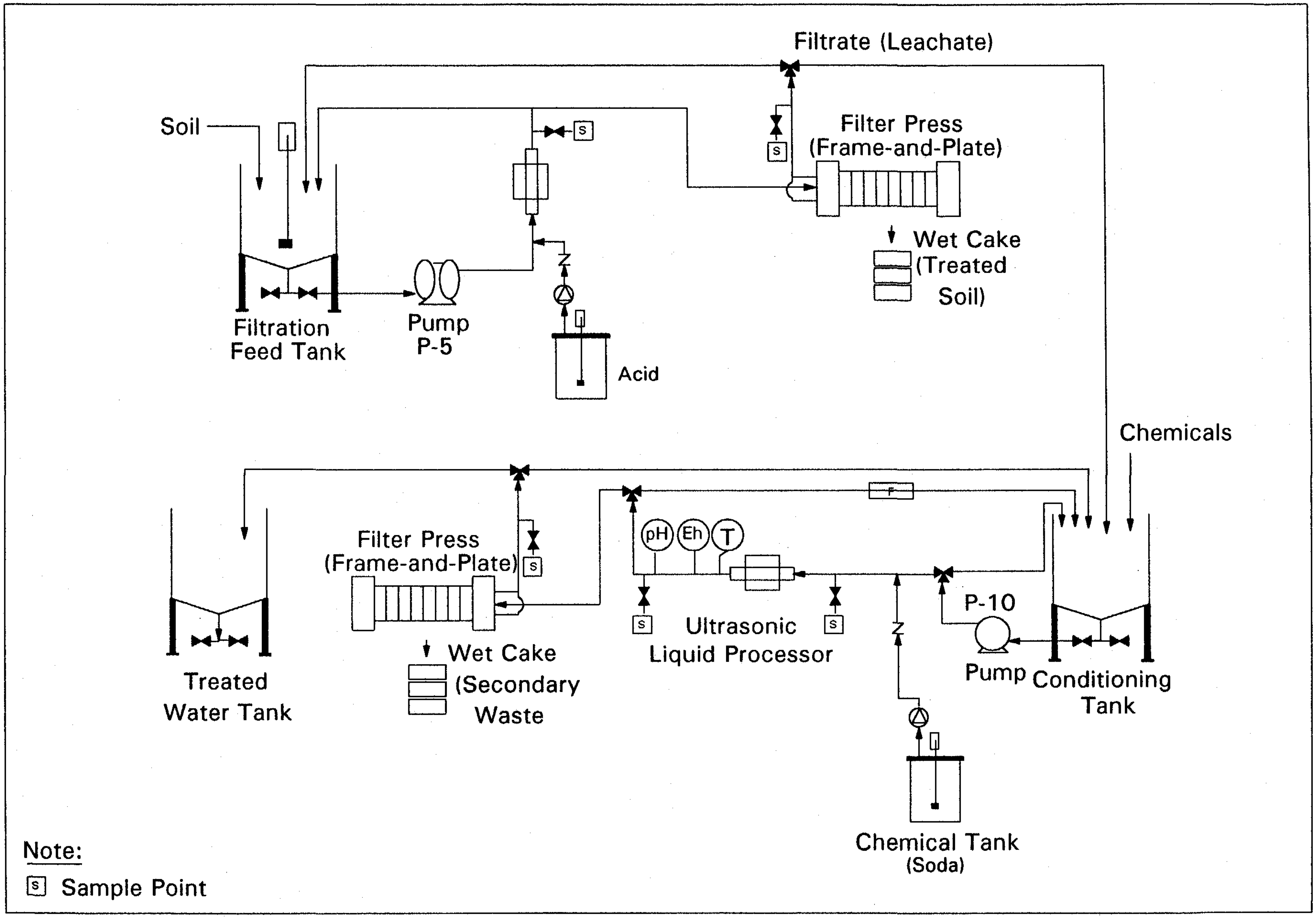


Figure A.9: Test Configuration for Pilot-Scale Ex-situ Chalk River Chemical Pit Soil Leaching and Leachate Treatment in a Tubular Ultrasonic Liquid Processor

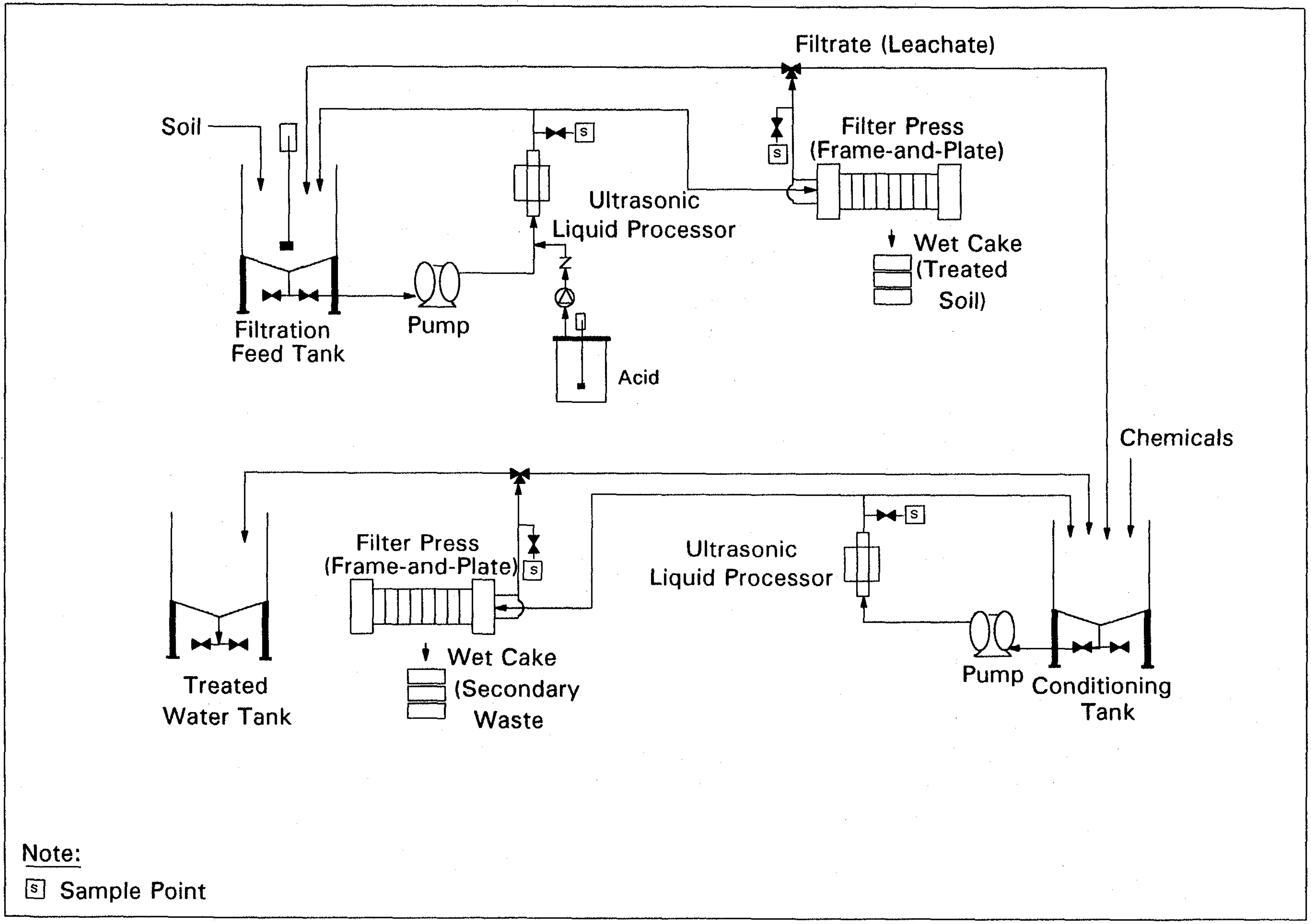


Figure A.10: Test Configuration for Pilot-Scale Ex-situ Fernald Incinerator Area Soil Leaching and Leachate Treatment Using a Tubular Ultrasonic Processor

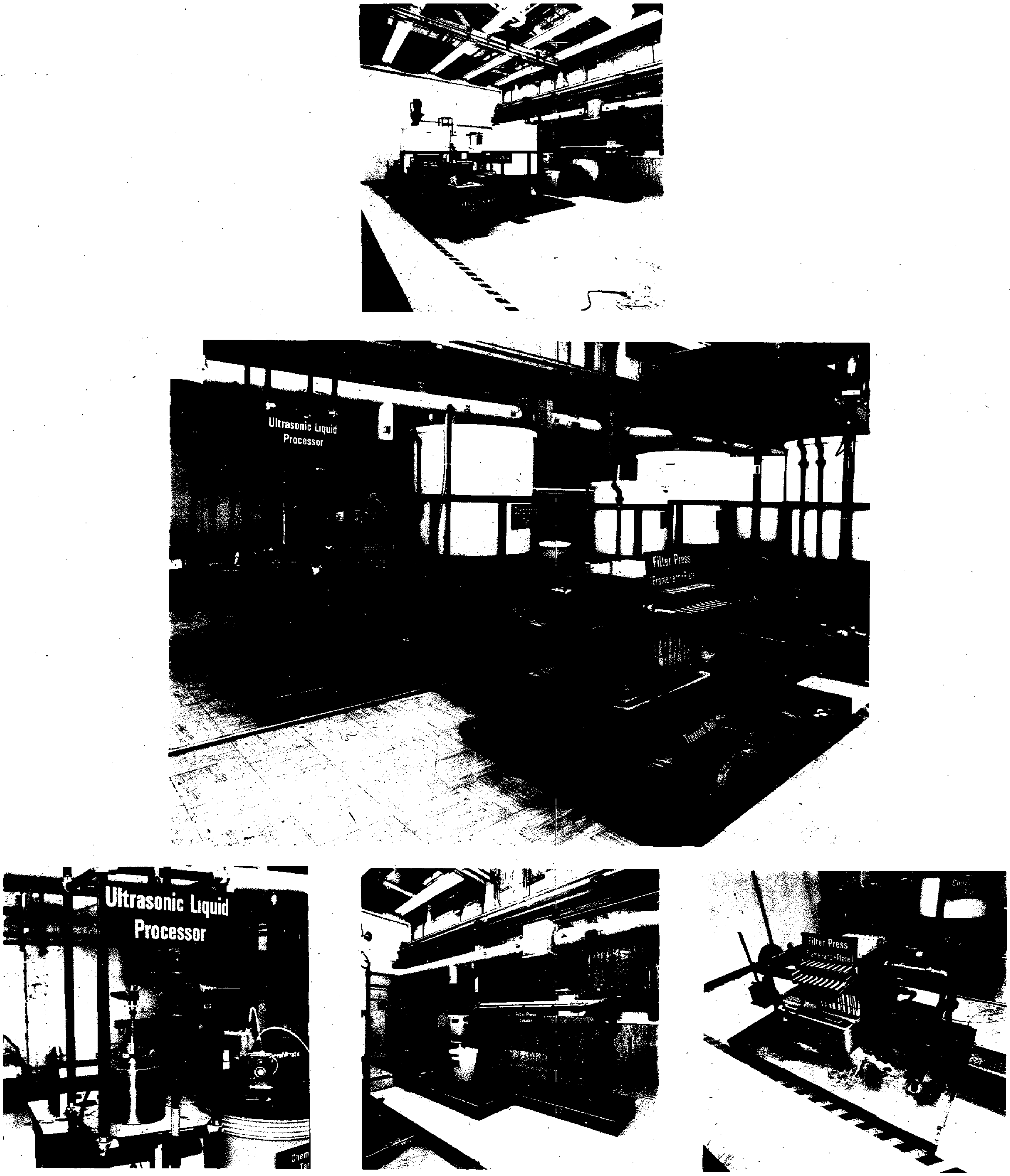


Figure A.11: Photographic Views of Pilot-scale Ex-situ Soil Leaching and Leachate Treatment System

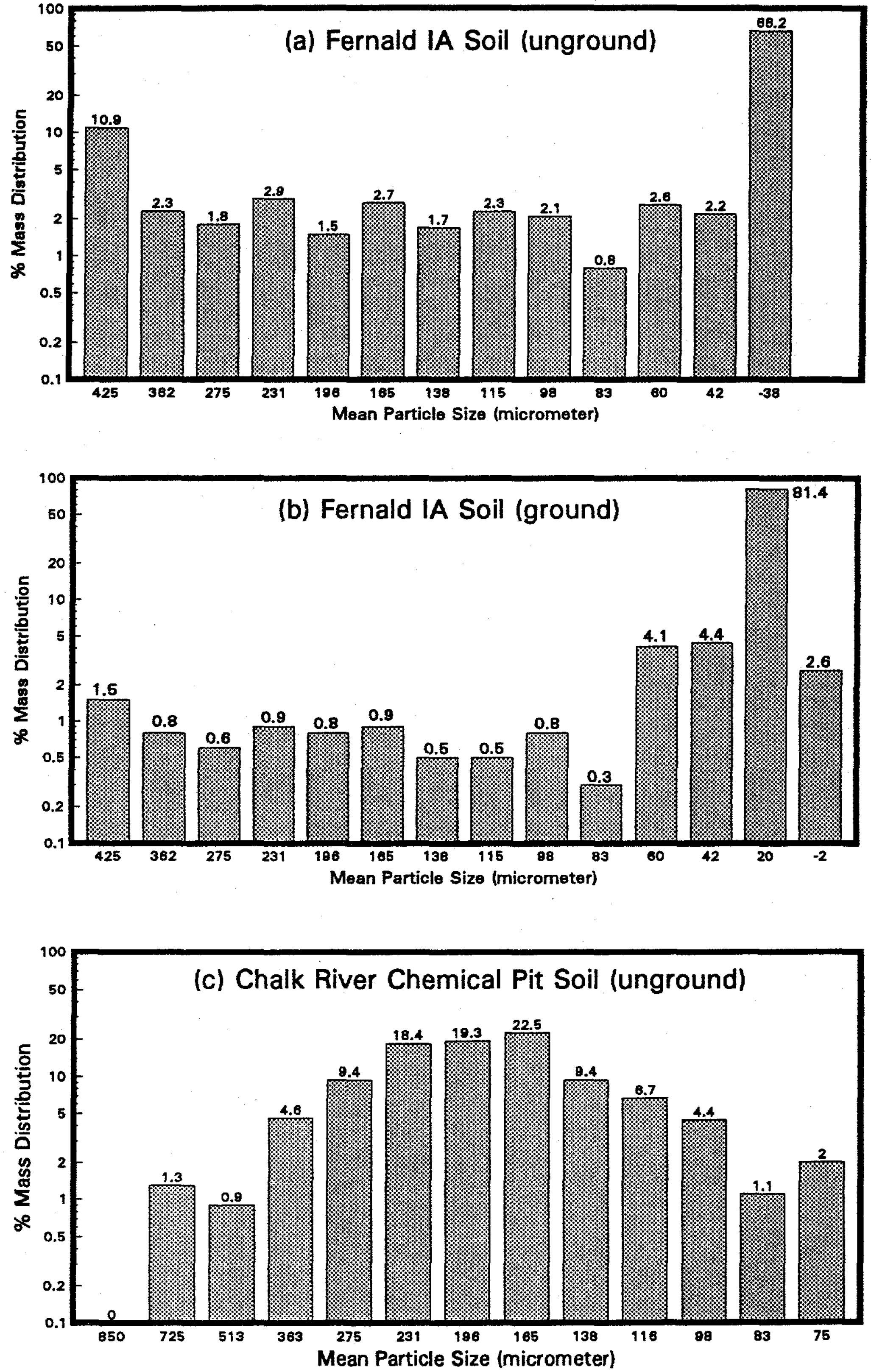


Figure A.12: Particle Size Distribution for Untreated Fernald Incinerator Area (IA) and Chalk River Chemical Pit Soils

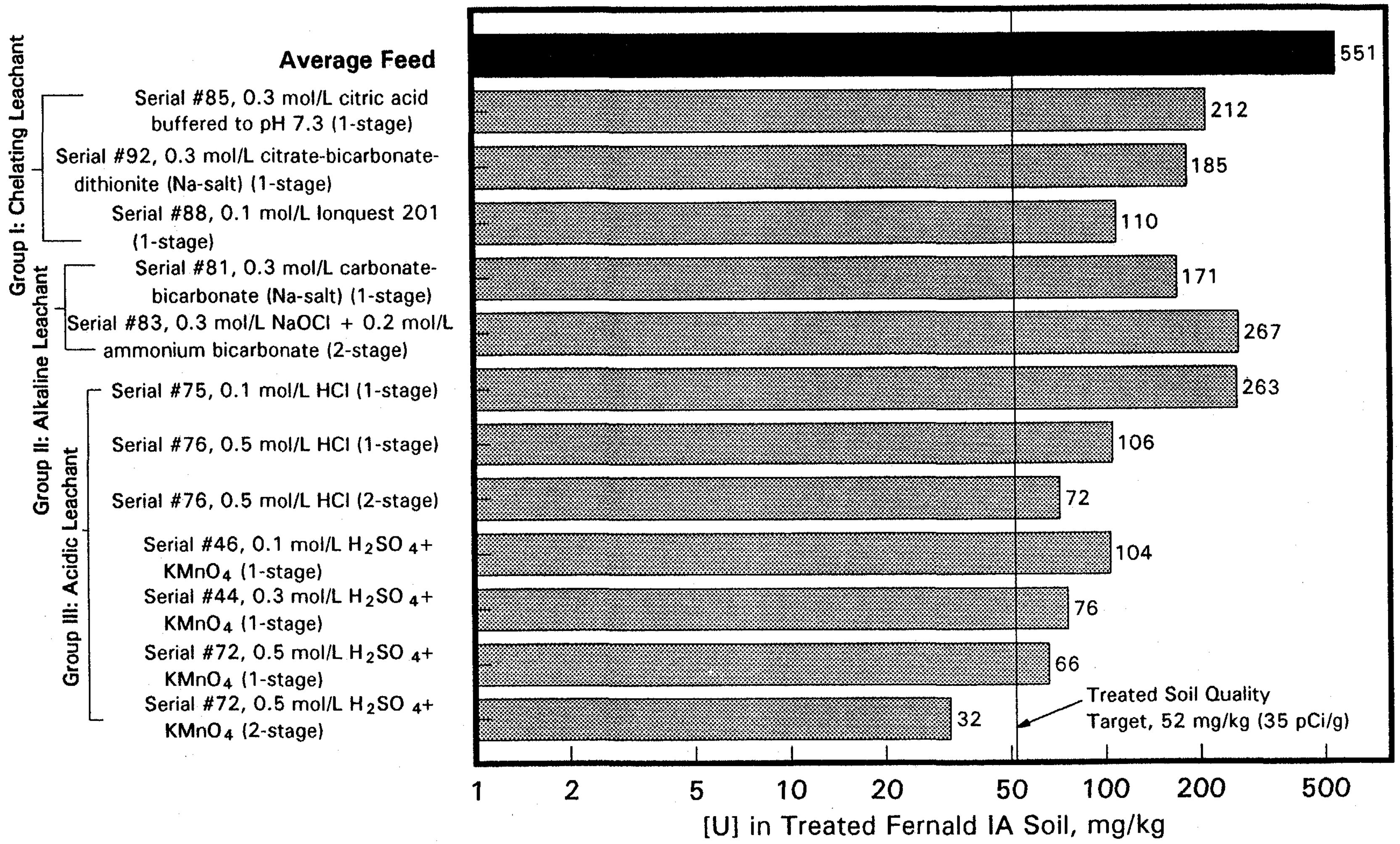


Figure A.13: Ultrasonically-Aided Leaching Performance for Fernald Incinerator Area Soil - Effect of Leachant and Leaching Condition on Uranium Removal

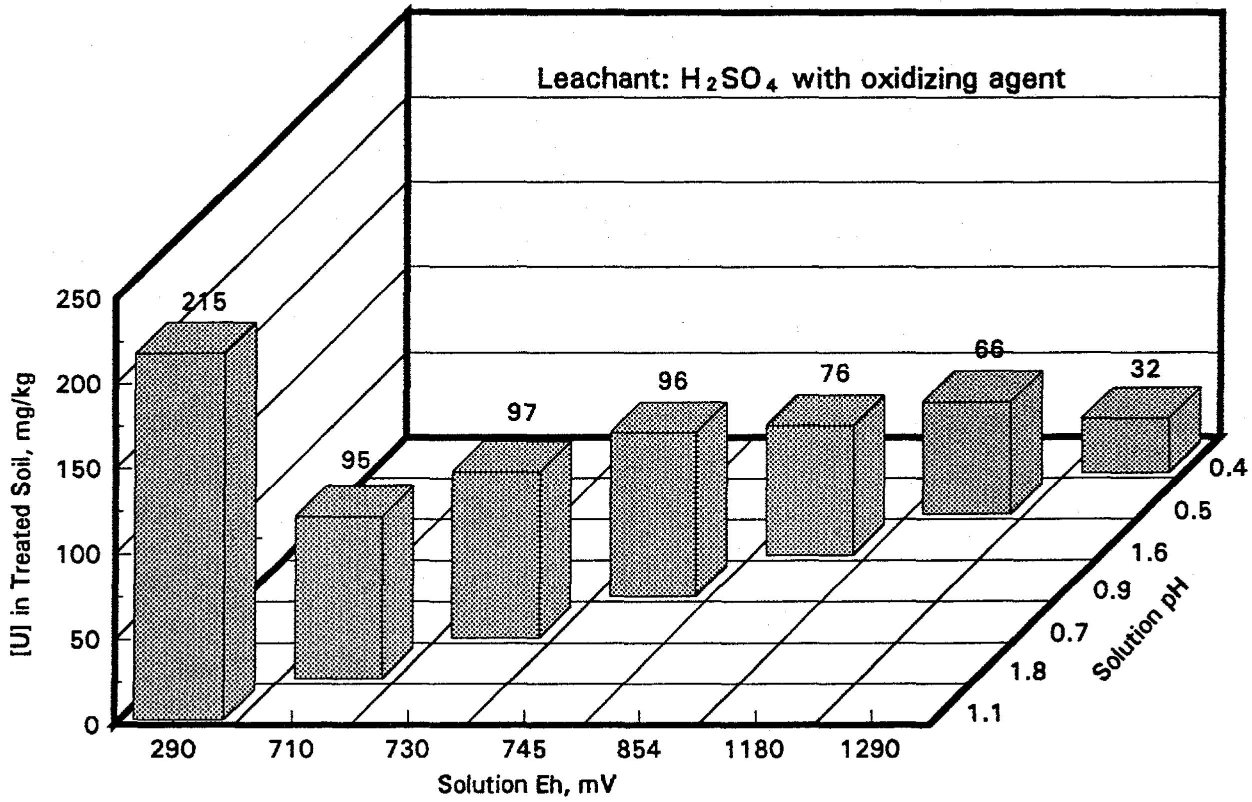


Figure A.14: Ultrasonically-Aided H2SO4 Leaching Performance for Fernald Incinerator Area Soil - Effect of Solution pH and Eh on Uranium Removal

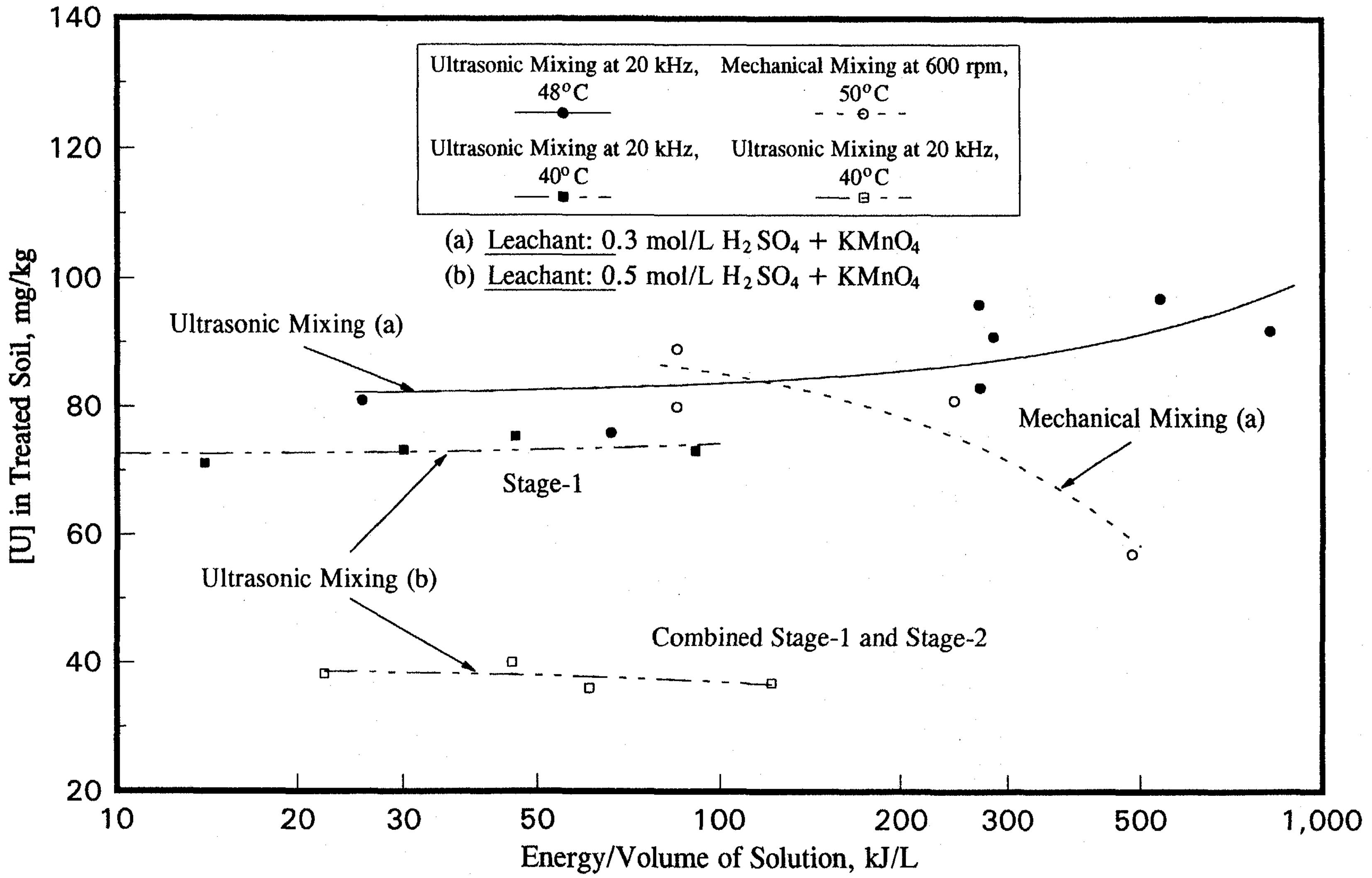
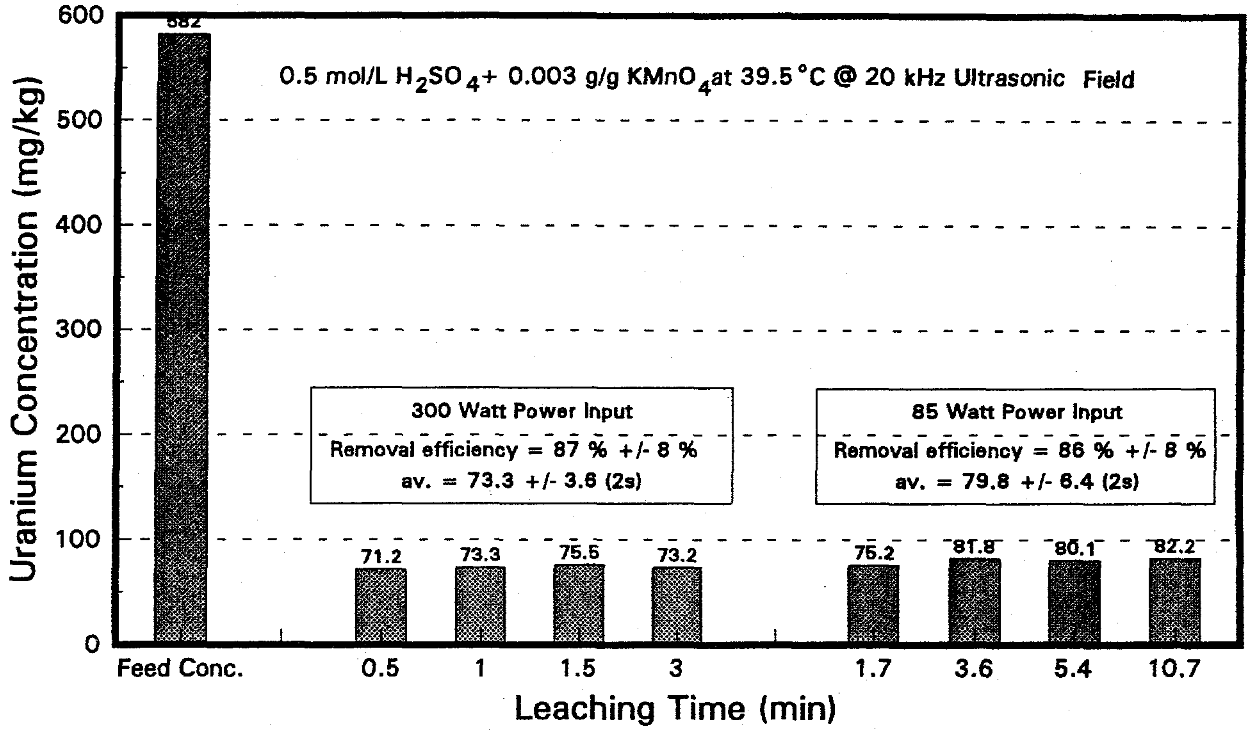


Figure A.15: Leaching Performance for Fernald Incinerator Area Soil - Effect of Mixing Mode and Mixing Energy Input on Uranium Removal

Single-Stage Leaching



Two-Stage Leaching

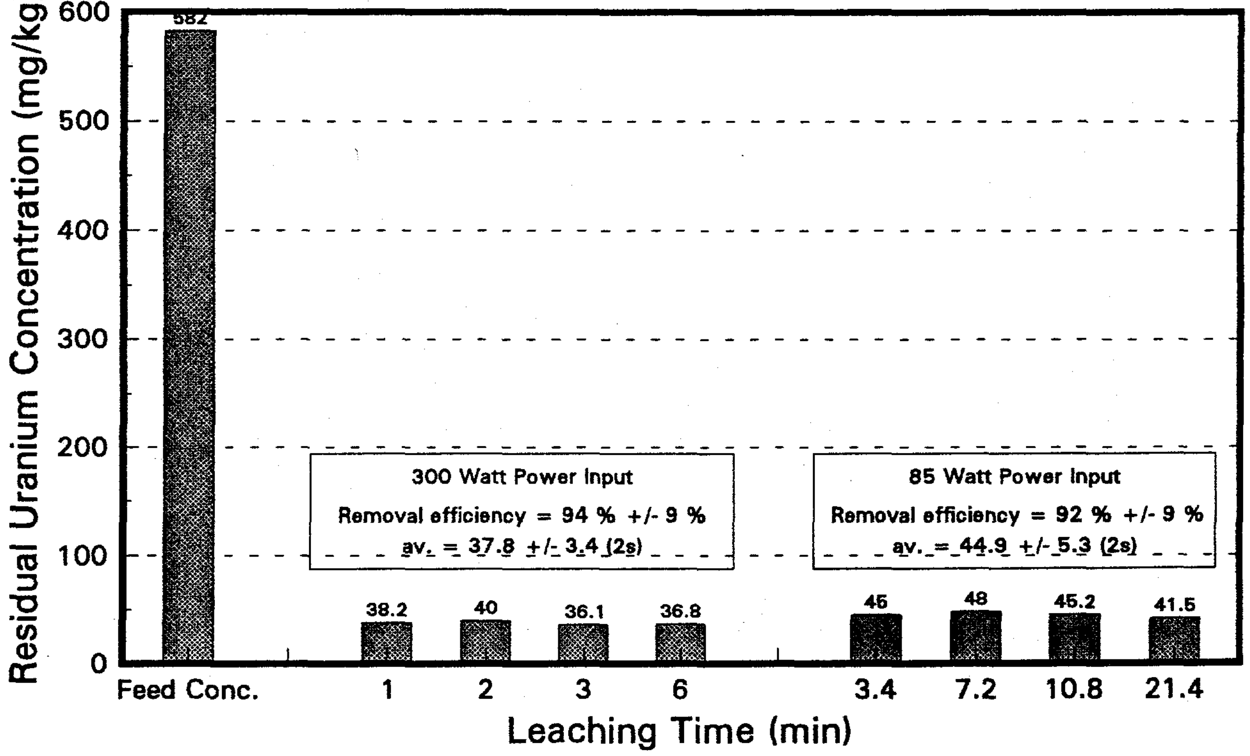


Figure A.16: Power-Time-Leaching Stage Effects on Uranium Removal from Fernald Incinerator Area soil (Bench-scale Ex-situ leaching tests) with 0.5 mol/L H_2SO_4 + $KMnO_4$.

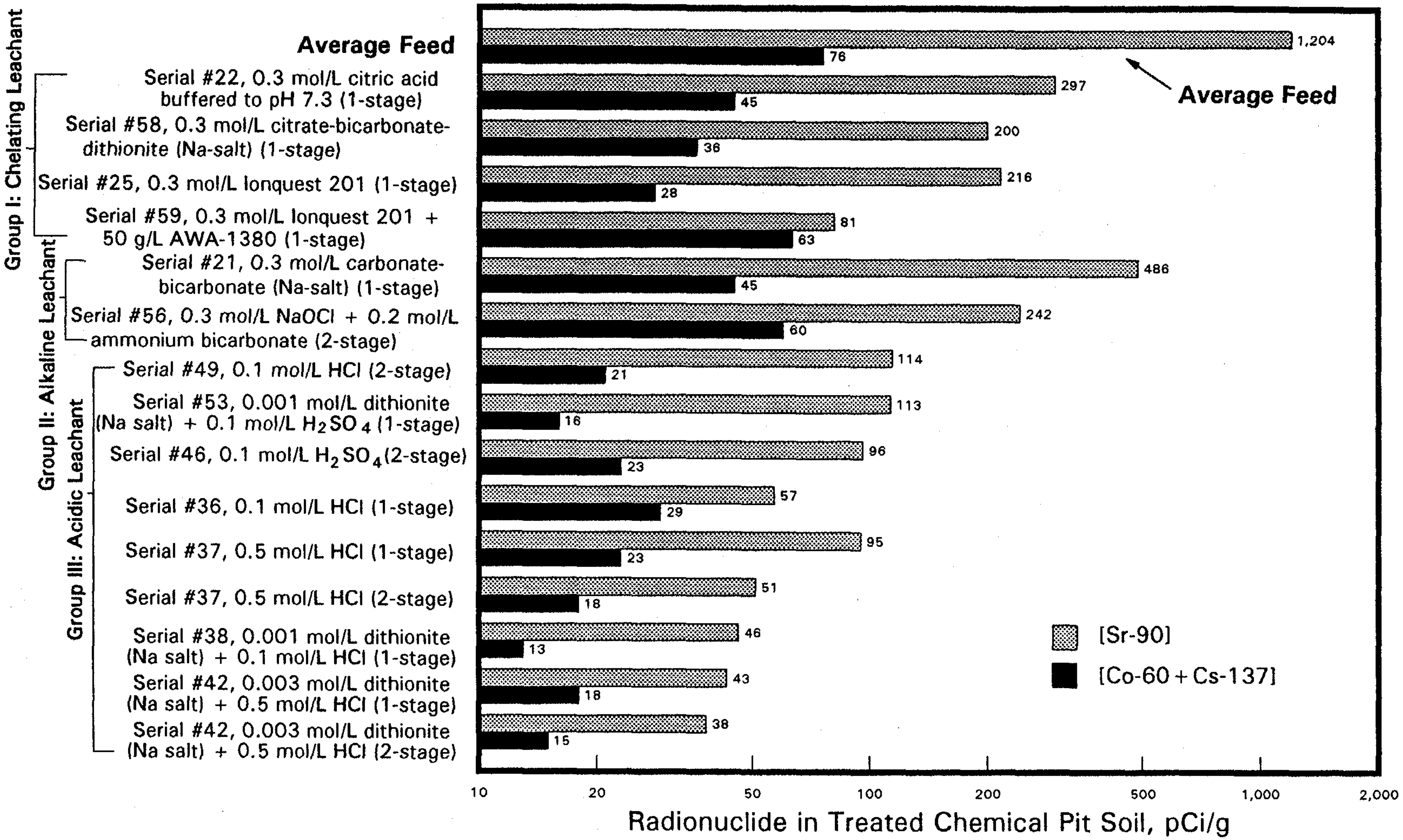


Figure A.17: Ultrasonic-Aided Leaching Performance for Chalk River Chemical Pit Soil - Effect of Leachant and Leaching Condition on Sr-90, Co-60 and Cs-137 Removal

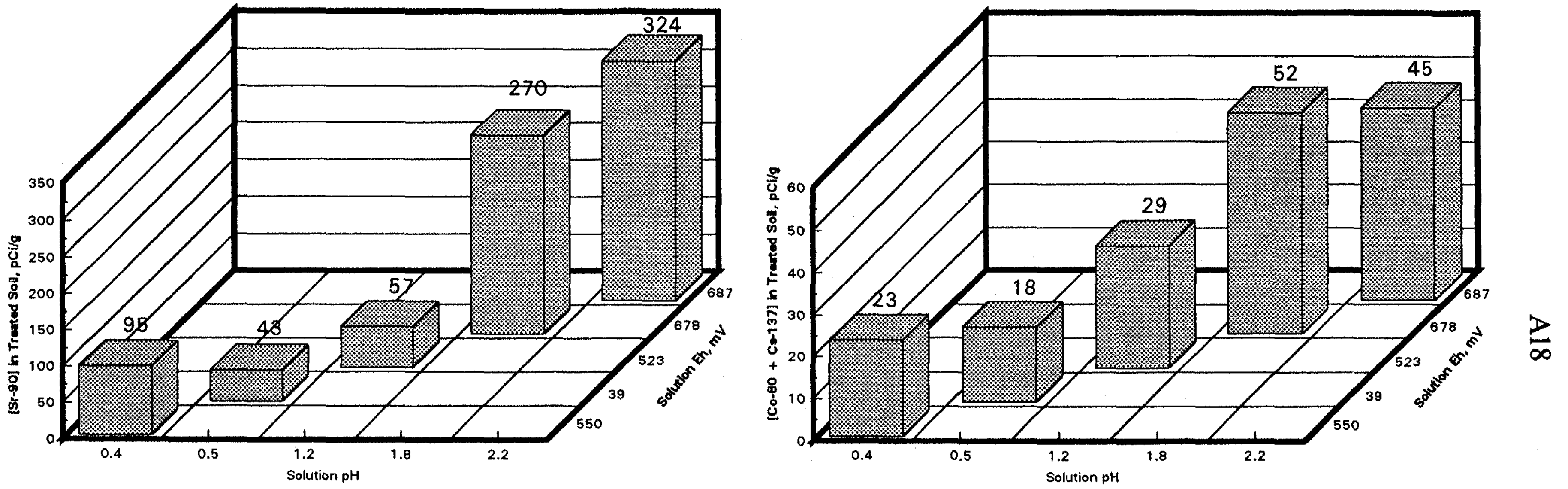


Figure A.18: Ultrasonically-Aided HCl Leaching Performance for Chalk River Chemical Pit Soil - Effect of Solution pH and Eh on Sr-90, Co-60 and Cs-137 Removal

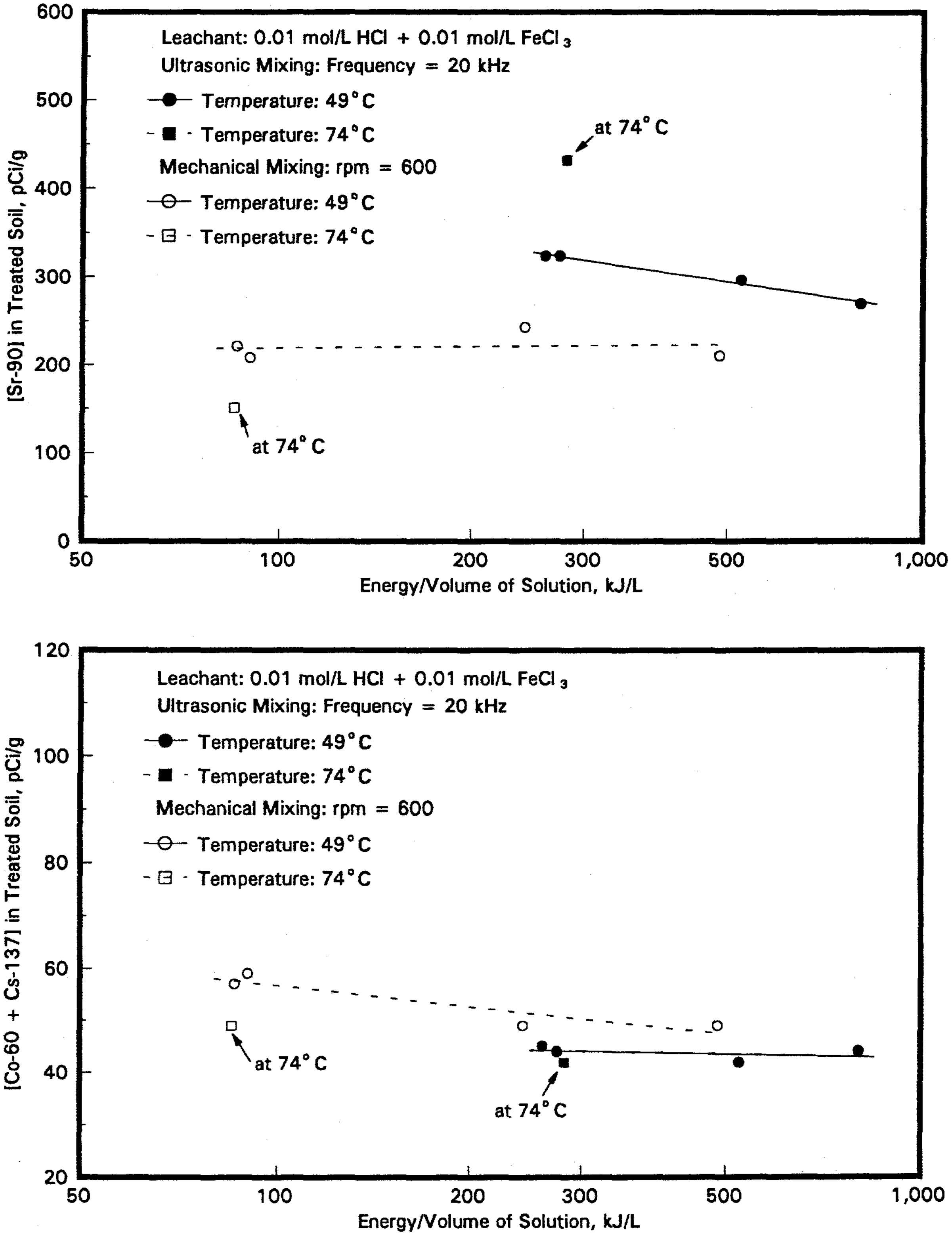


Figure A.19: Leaching Performance for Chalk River Chemical Pit Soil - Effect of Mixing Mode and Mixing Energy Input on Sr-90, Co-60 and Cs-137 Removal

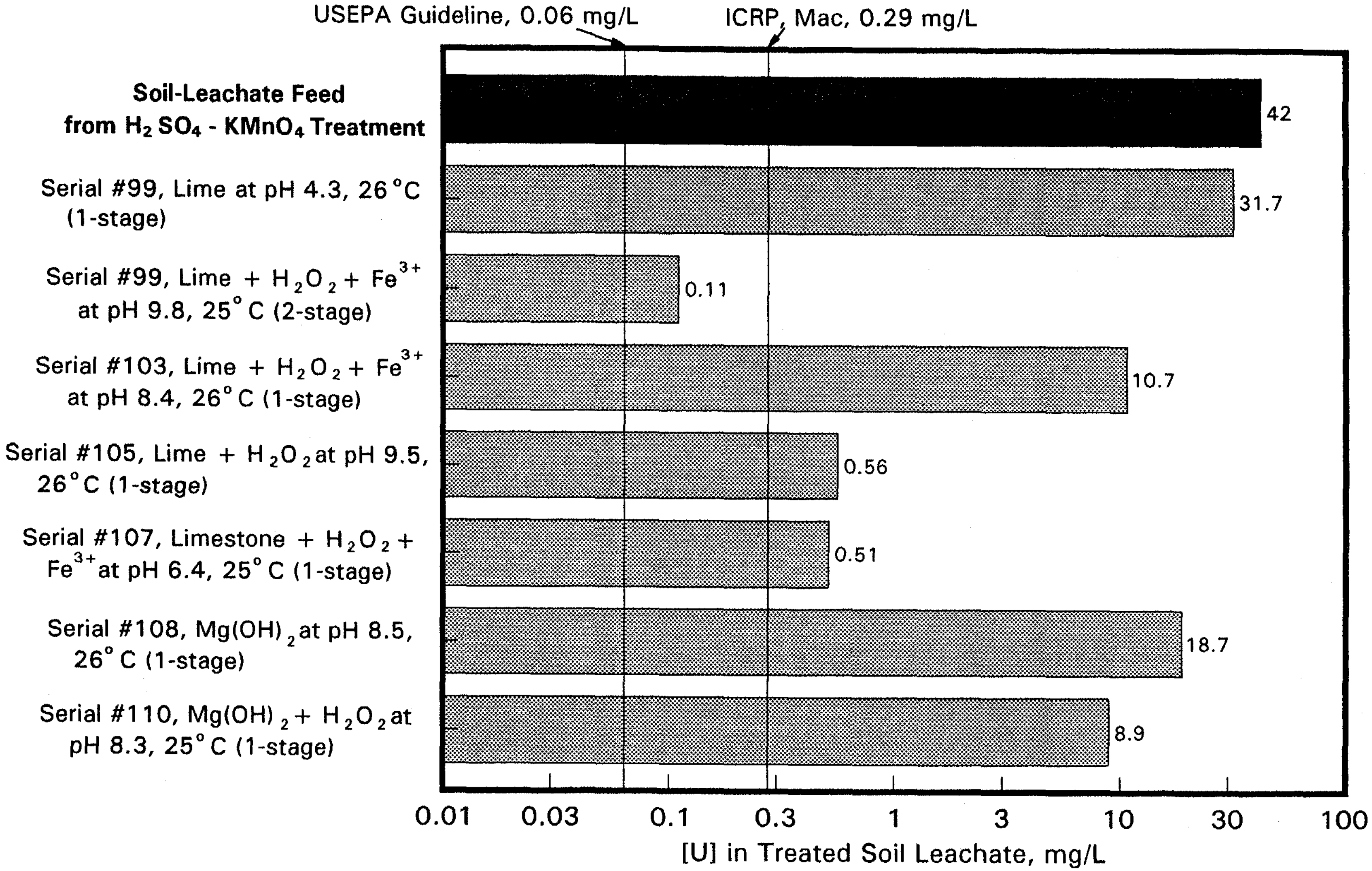


Figure A.20: Ultrasonically-Aided Leachate Treatment Performance for Fernald Incinerator Area Soil - Effect of Precipitant and Sorbent on Uranium Removal

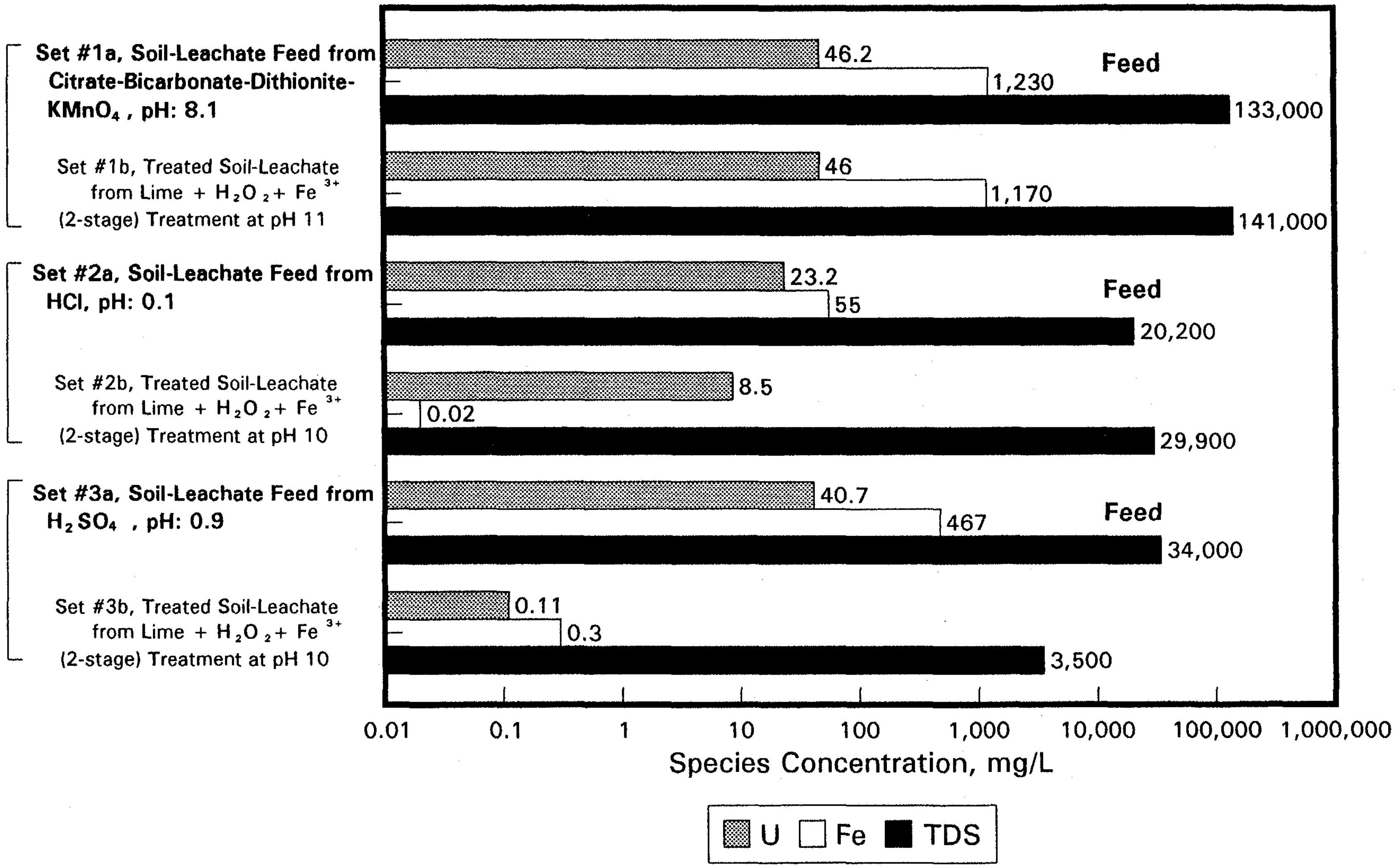


Figure A.21: Fernald Incinerator Area Soil-Leachate Treatment - Effect of Ultrasonically-Aided Chemical Treatment at 25° C on U, Fe and TDS Removal

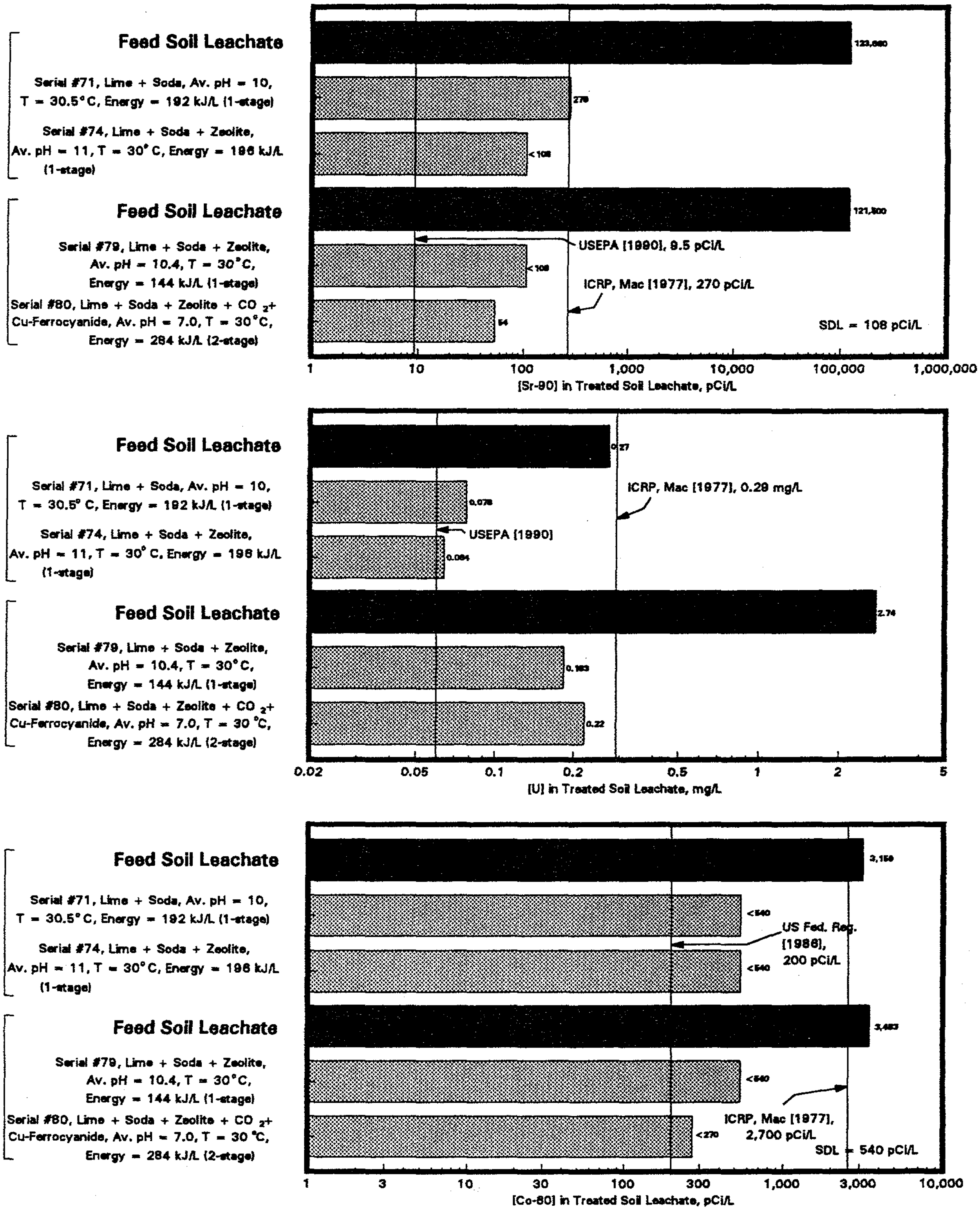


Figure A.22: Ultrasonically-Aided Leachate Treatment Performance for Chalk River Chemical Pit Soil - Effect of Precipitant and Sorbent on Sr-90, U and Co-60 Removal

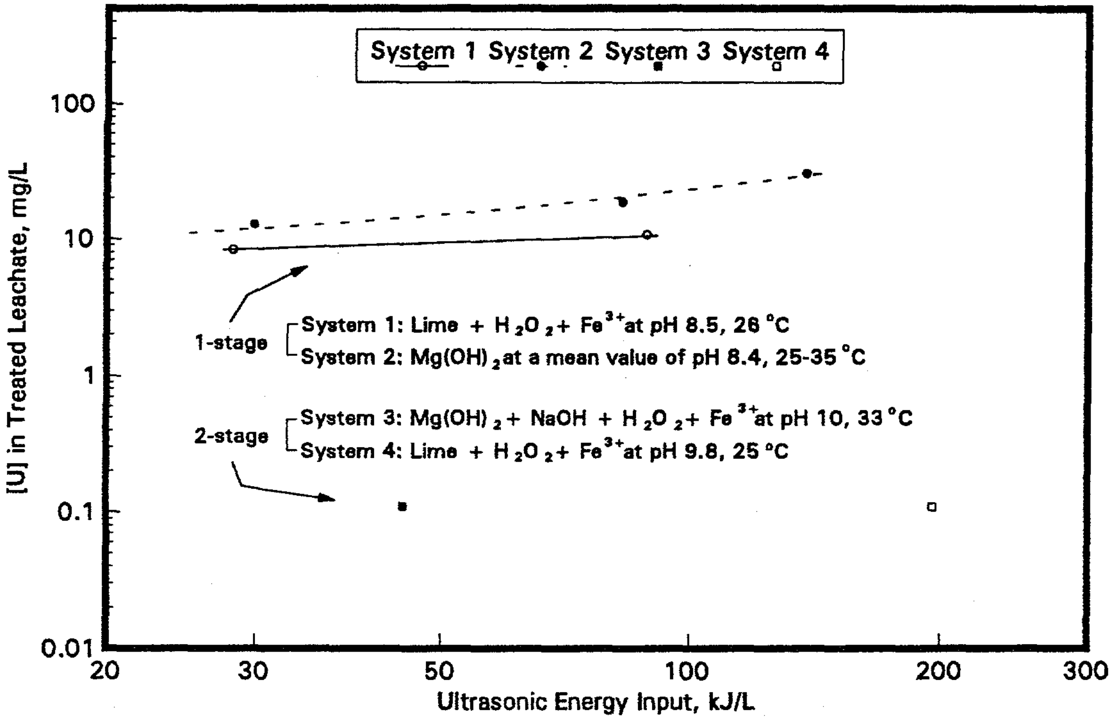


Figure A.23: Soil-Leachate Treatment Performance for Fernald Incinerator Area Soil - Effect of Ultrasonic Mixing Energy Input on Uranium Removal

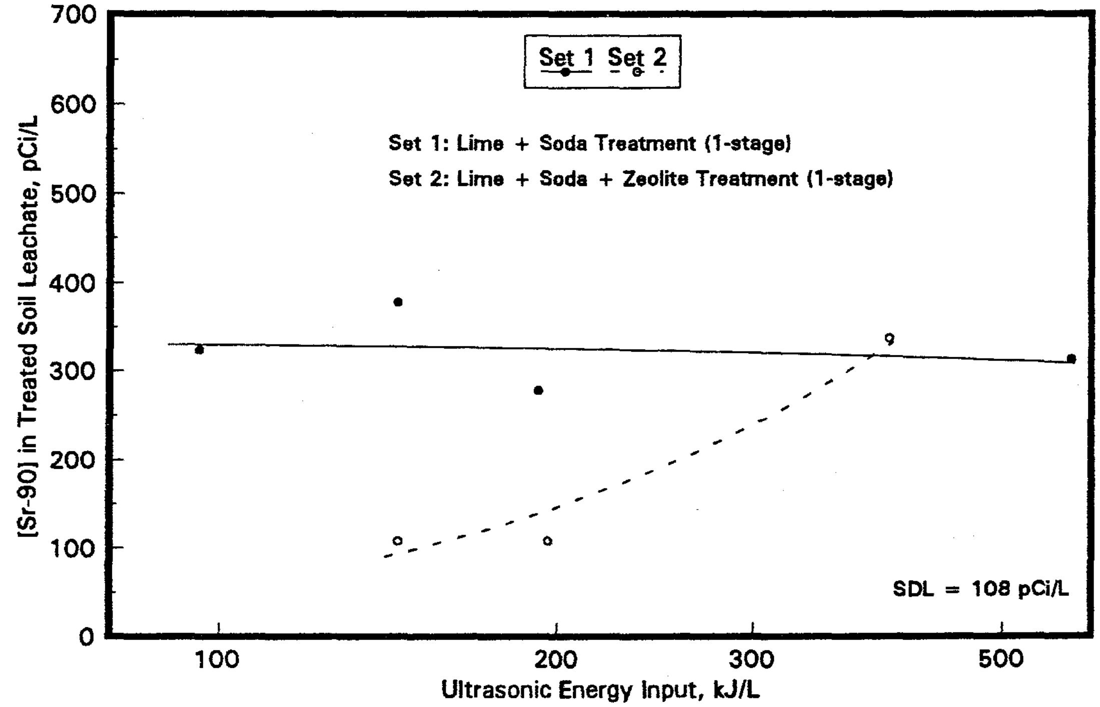


Figure A.24: Soil-Leachate Treatment Performance for Chalk River Chemical Pit Soil - Effect of Ultrasonic Mixing Energy Input on Sr-90 Removal

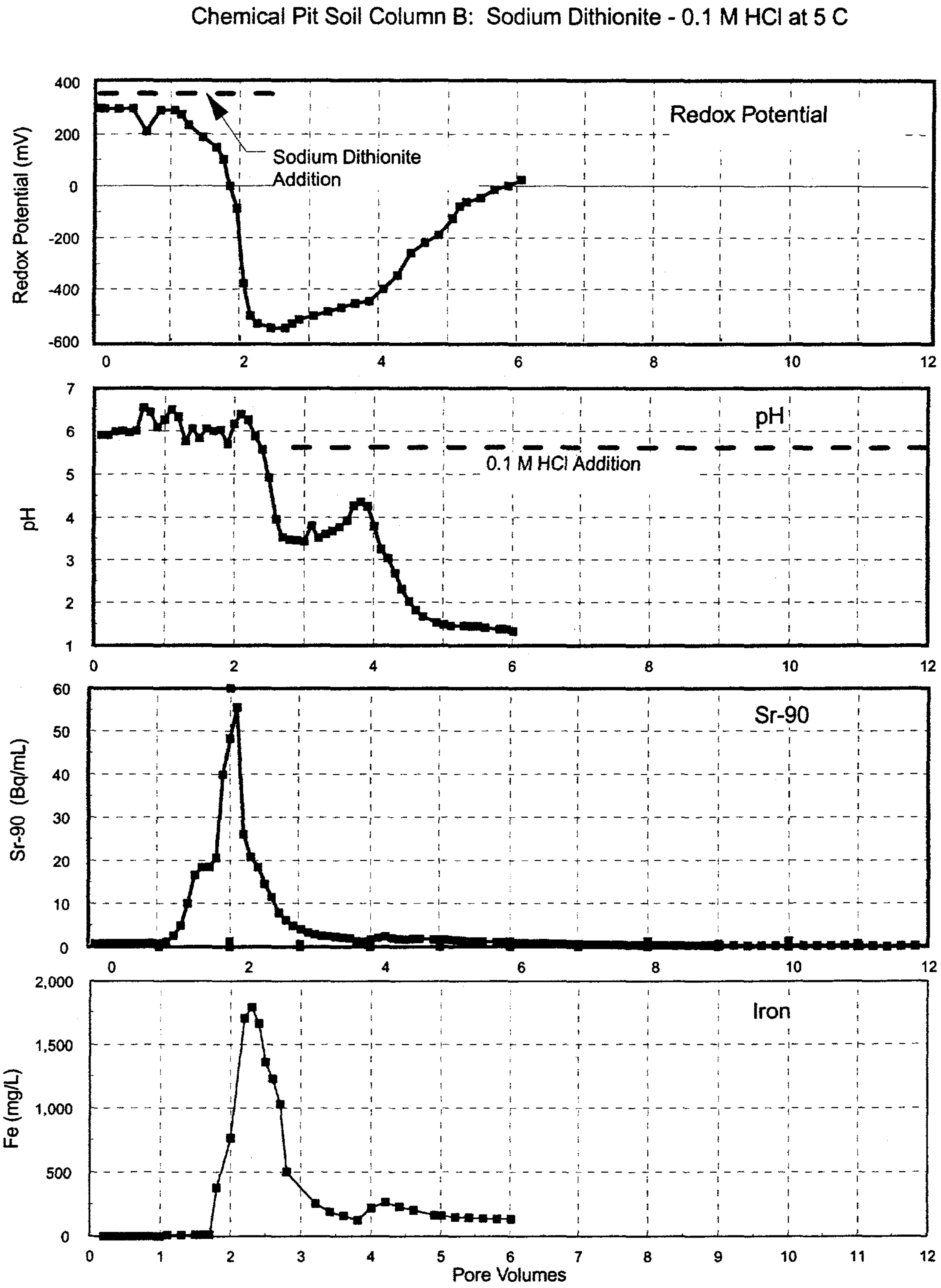


Figure A.25: Soil Column B Effluent Redox Potential, pH, Sr-90, and Fe Concentrations versus Pore Volumes of Eluent

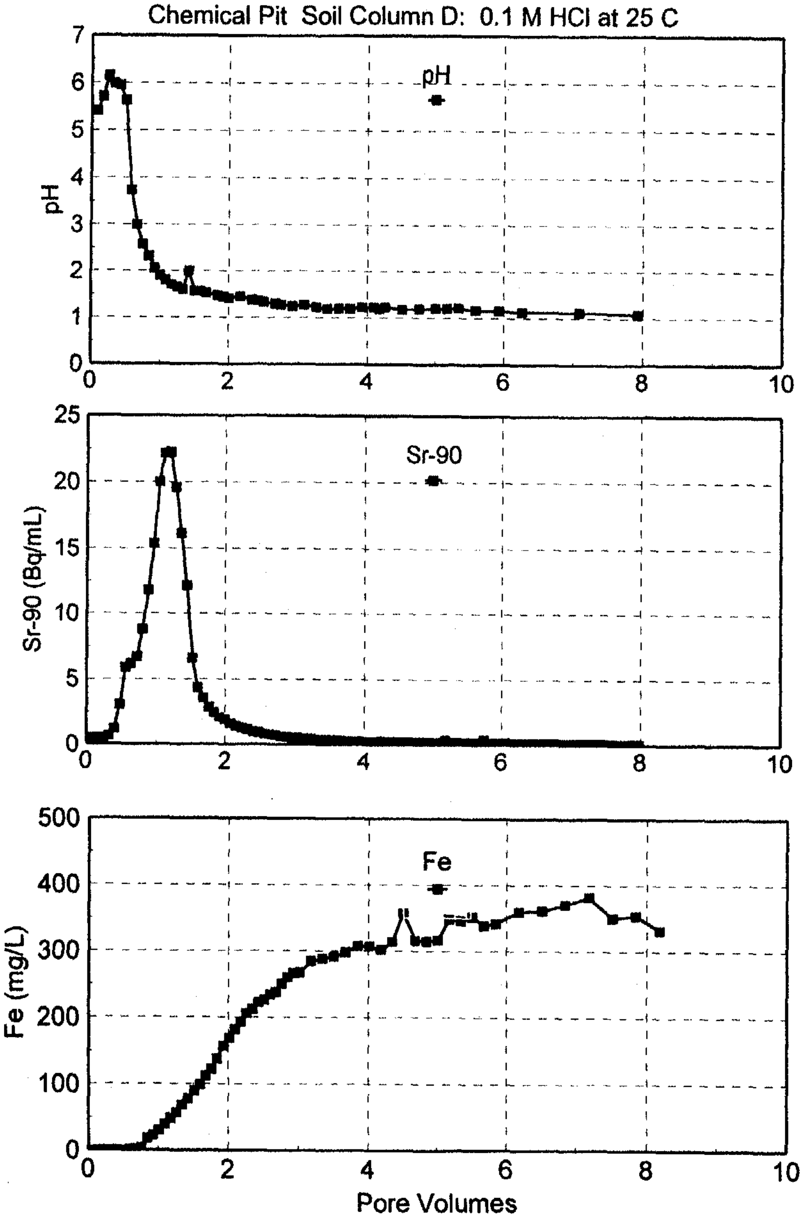


Figure A.26: Soil Column D Effluent pH, Sr-90 and Fe Concentrations versus Pore Volumes of Eluent

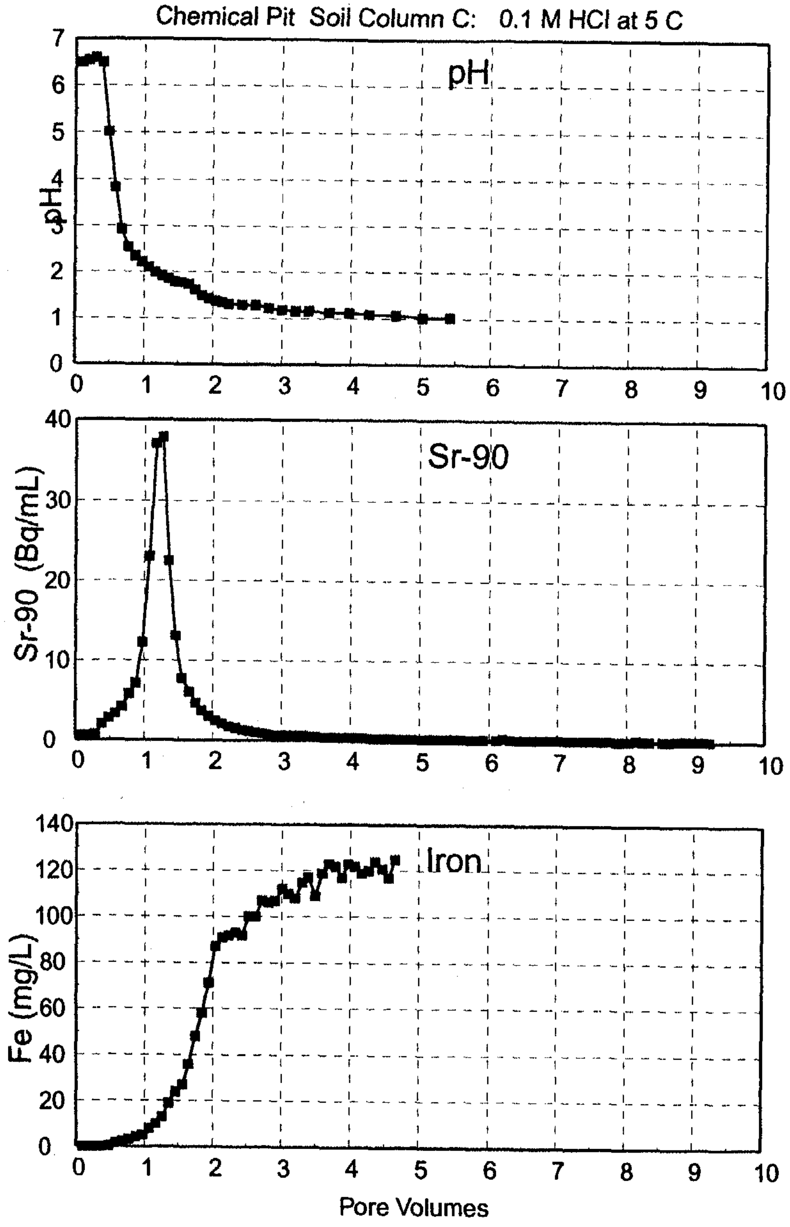


Figure A.27: Soil Column C Effluent pH, Sr-90, and Fe Concentrations versus Pore Volumes of Eluent

Chemical Pit in Situ Leach Test

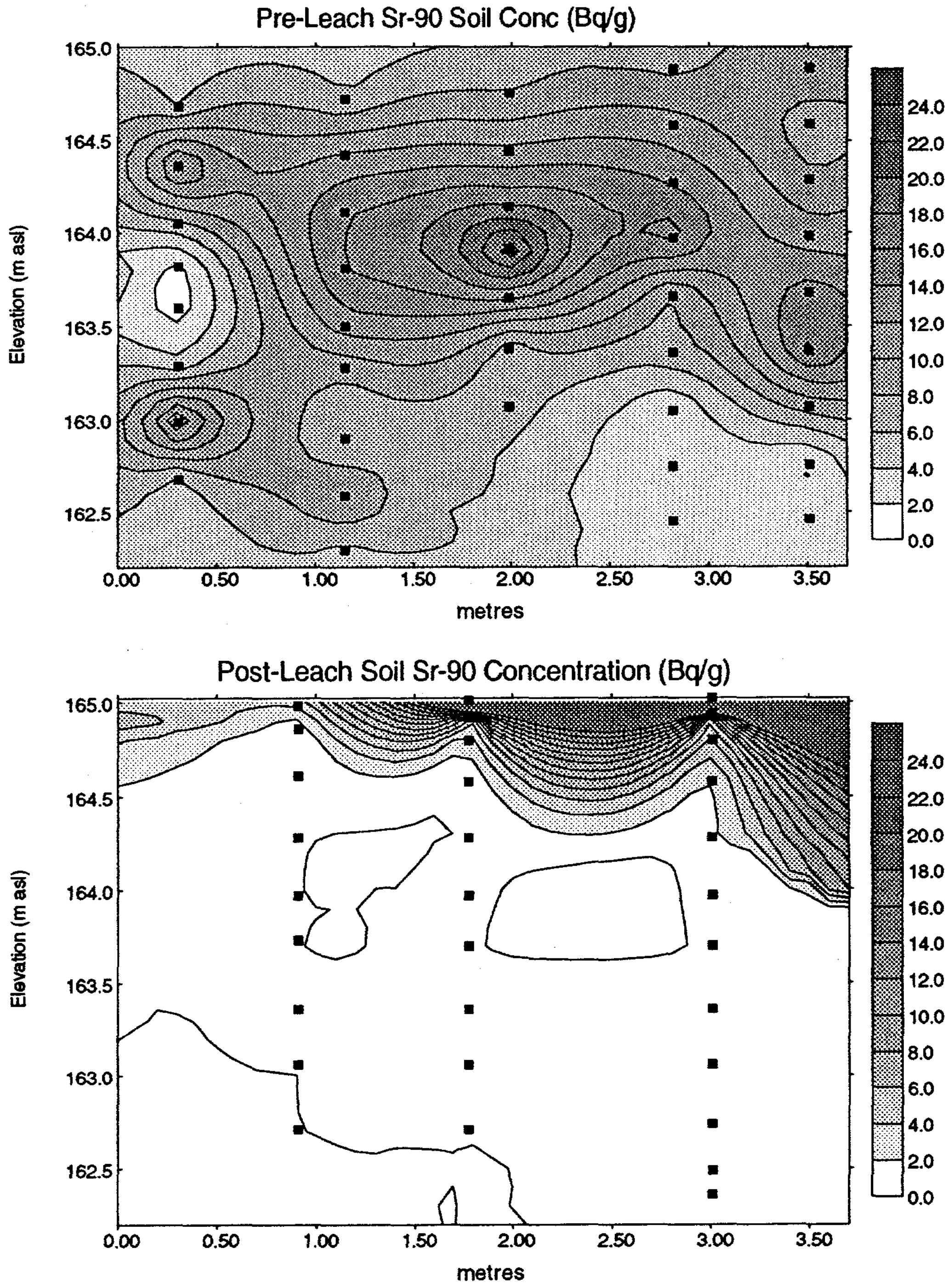
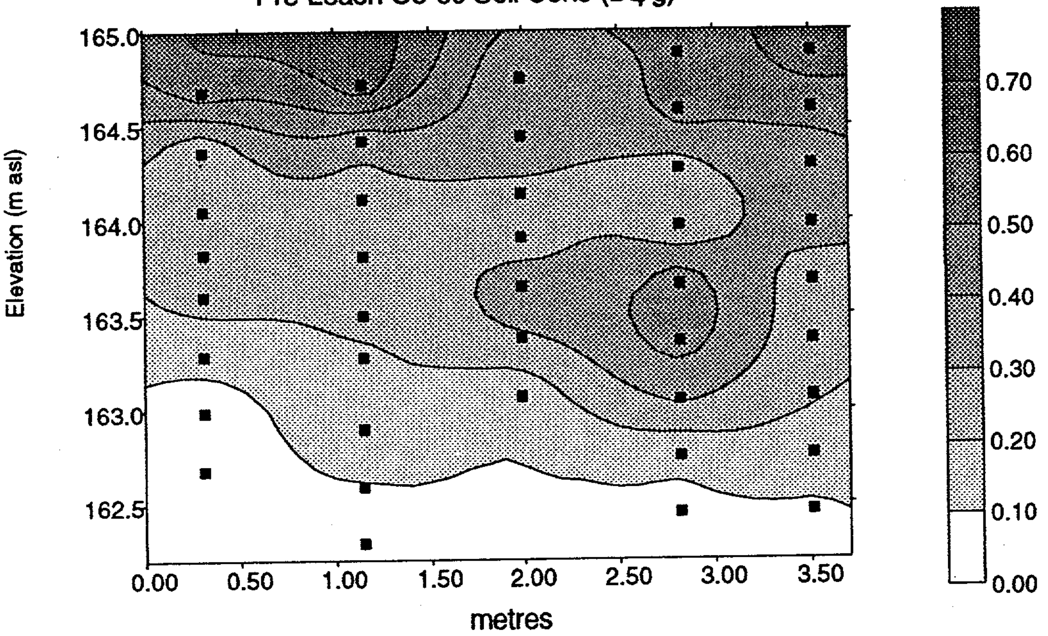


Figure A.28: Distribution of Sr-90 in the Test Cell Before and After the Leaching Test, Based on Soil Analyses

Chemical Pit in Situ Leach Test

Pre-Leach Co-60 Soil Conc (Bq/g)



Final Co-60 Soil Conc (Bq/g)

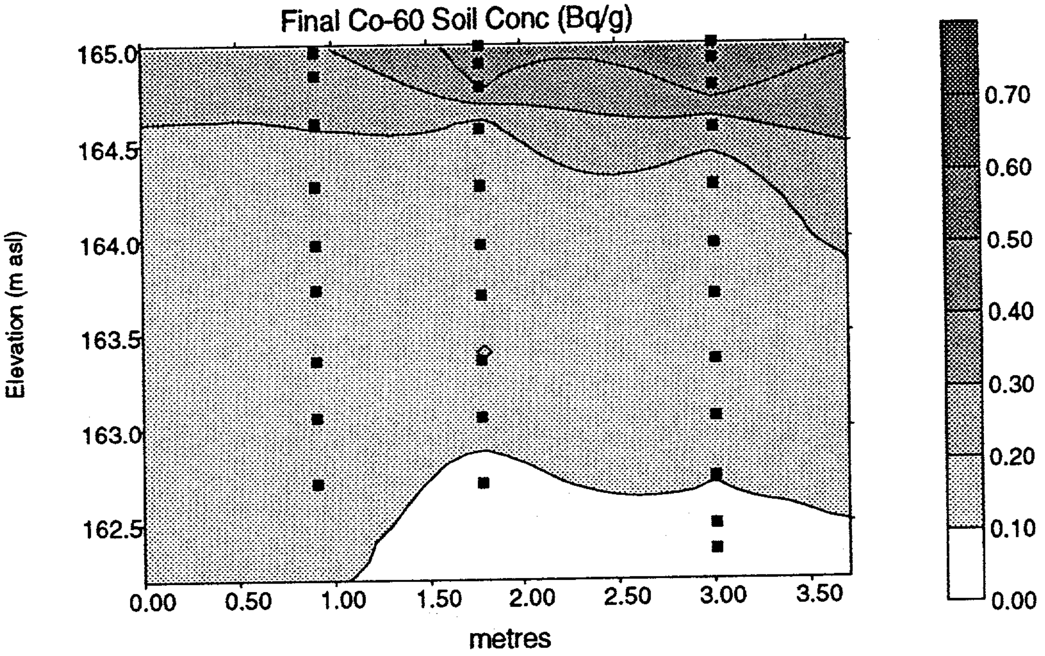


Figure A.29: Distribution of Co-60 in the Test Cell Before and After the Leaching Test, Based on Soil Analyses

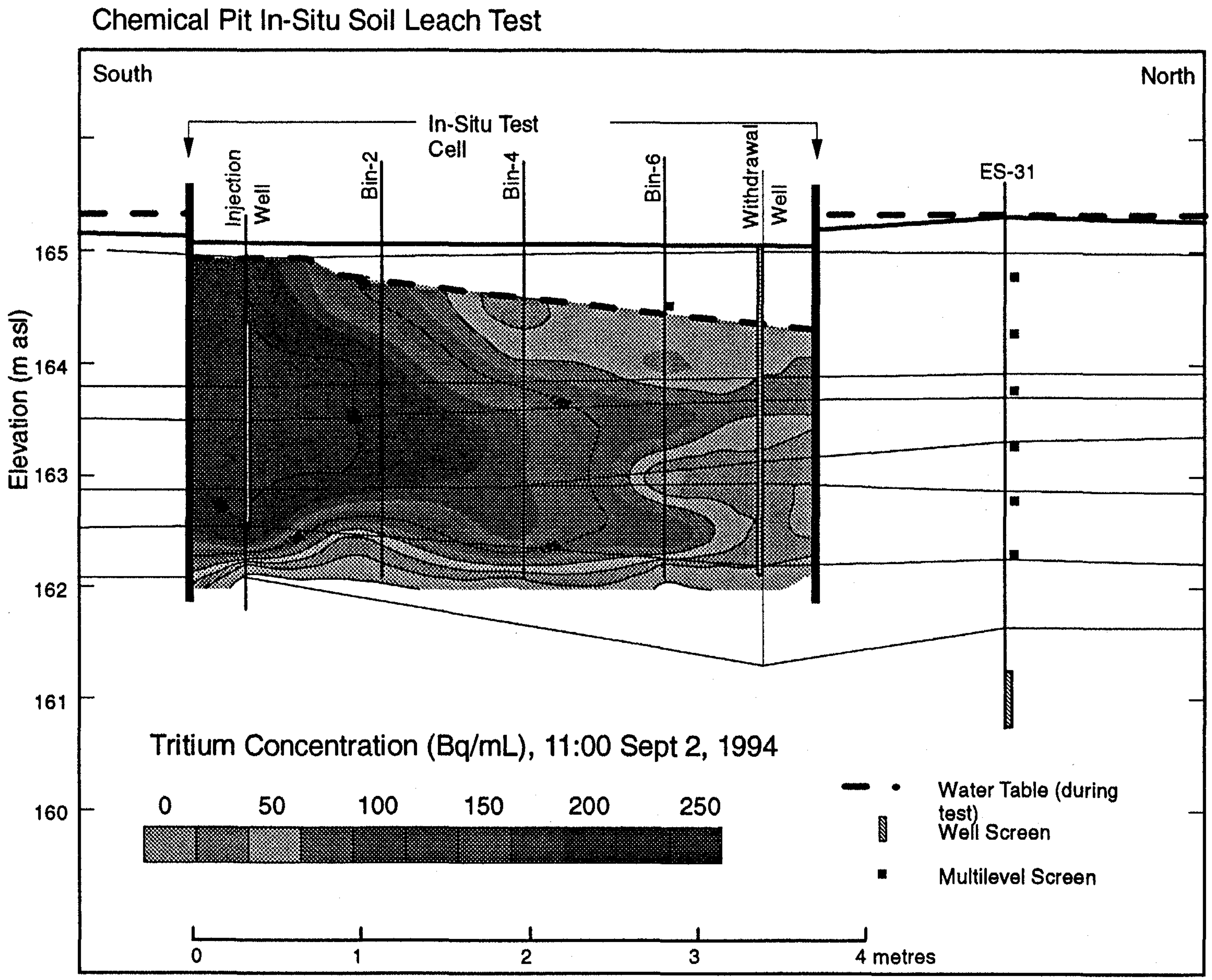
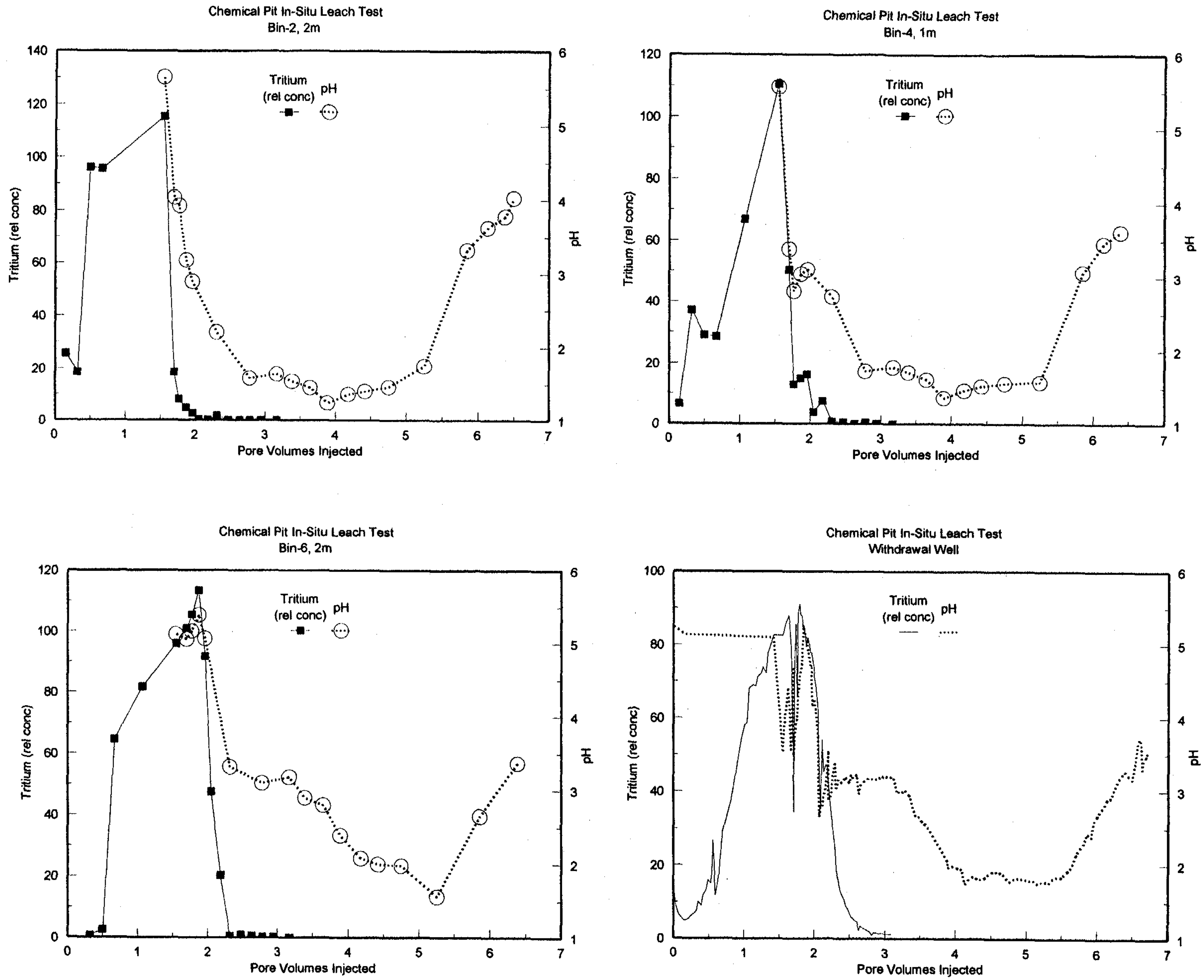


Figure A.30: Tritium concentration in Longitudinal Cross Section at 11:00, 1194 September 2



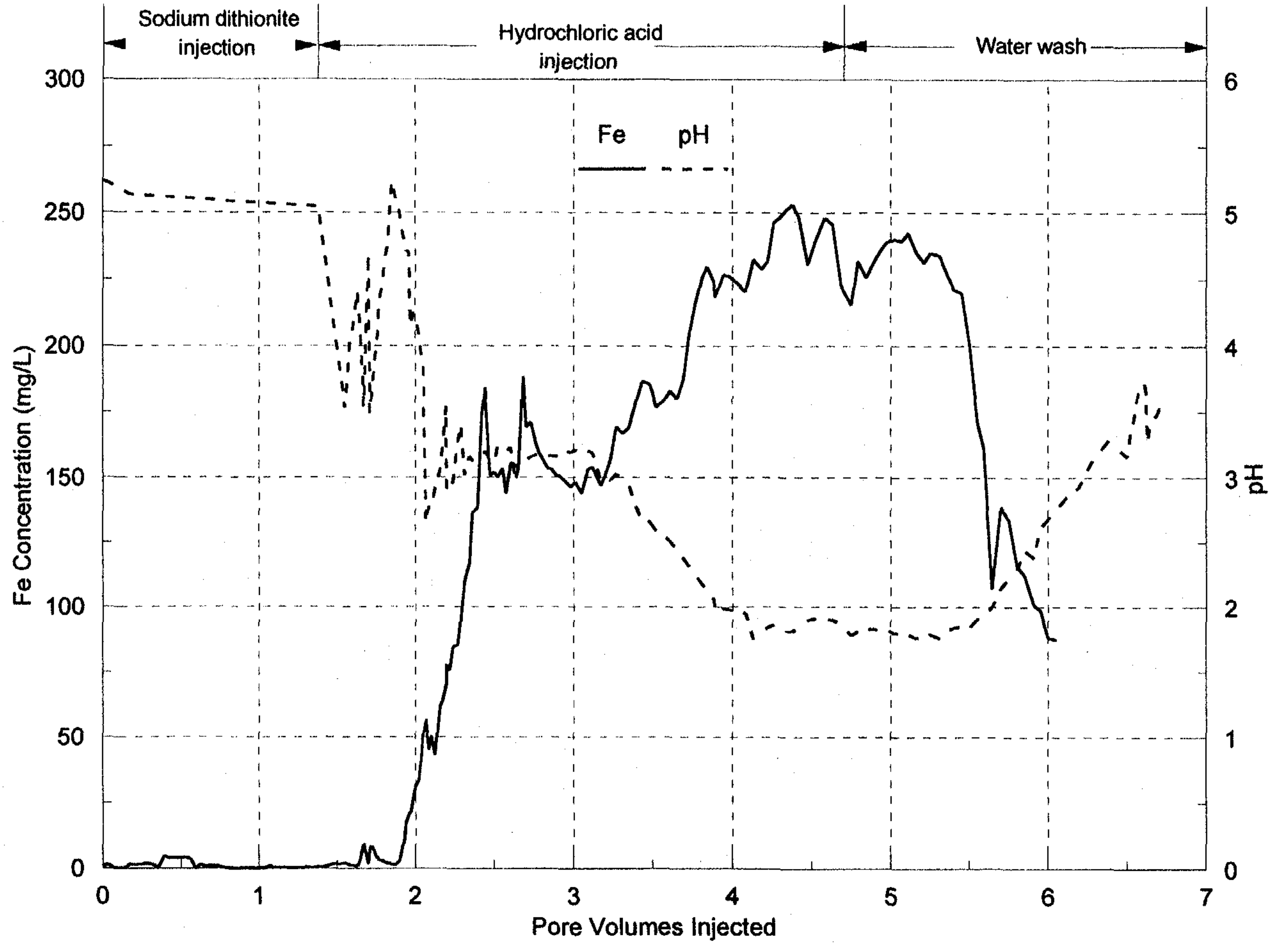
Chemical Pit In-Situ Leach Test
Bin-2, 2m

Chemical Pit In-Situ Leach Test
Bin-4, 1m

Chemical Pit In-Situ Leach Test
Bin-6, 2m

Chemical Pit In-Situ Leach Test
Withdrawal Well

Figure A.31 Tritium Concentrations and pH versus Pore Volumes Injected, Measured 0.8, 1.7, 2.5, and 3.1 m from the Injection Well



Notes:
1) Number of pore volumes of sodium dithionite solution injected : 1.34
2) Number of pore volumes of hydrochloric acid solution injected : 3.4
3) Number of pore volumtes of water injected after hydrochloric acid : 1.97
4) Average flowrate of solution injected : 570 mL/min [450 - 634 mL / min]
5) One pore volume : approximately 4100 L
6) Overall soil to liquid ratio: approximately 1 : 2

Figure A.32: In-situ Chalk River Soil Leaching: Measured pH and Fe Concentration in the Withdrawal Well

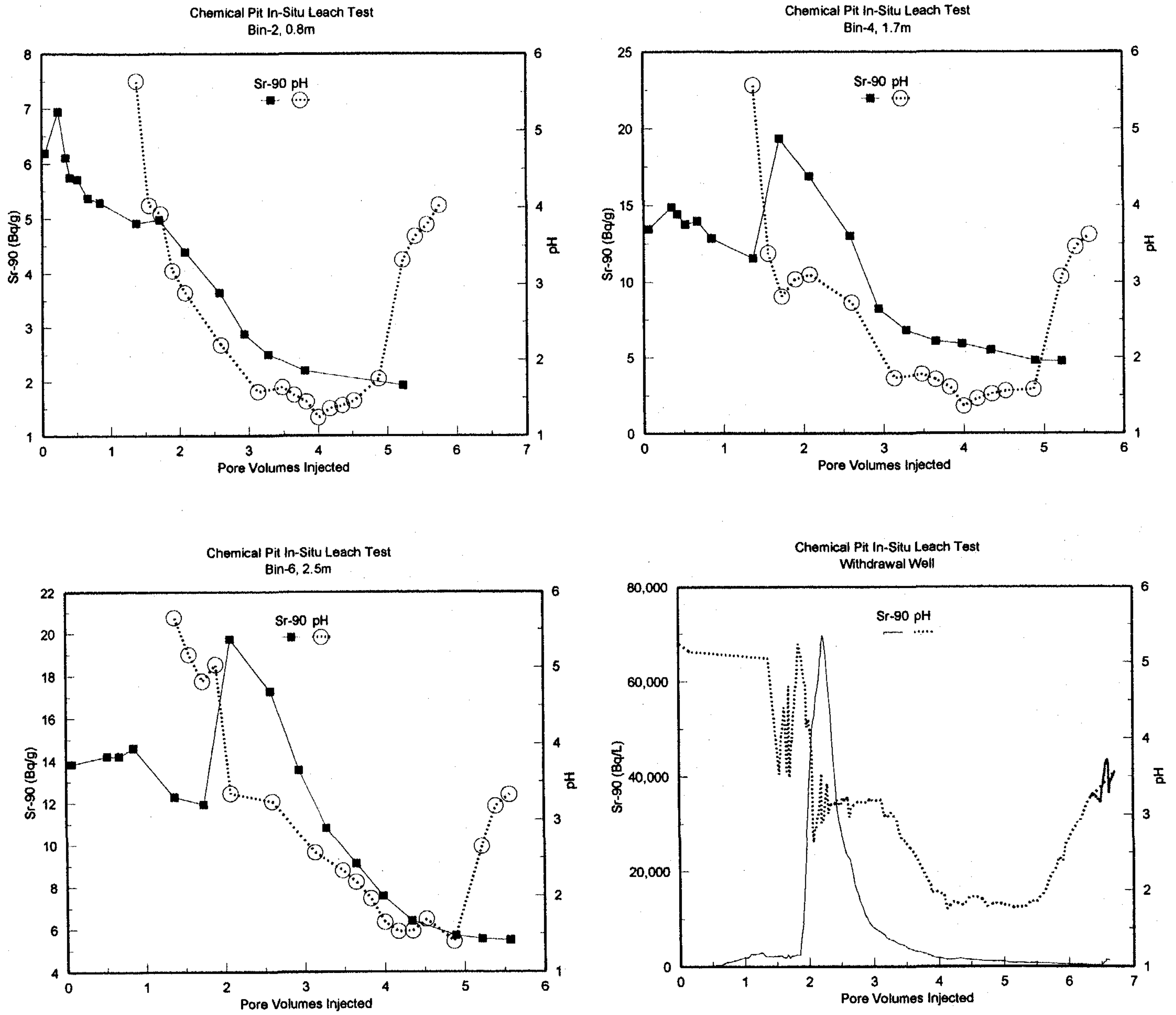


Figure A.33: Measured pH and Computed Sr-90 Concentrations at 0.8, 1.7 and 2.5 m from the Injection Well, and Measured Sr-90 Concentrations in the Withdrawal well, all Plotted Against pore Volumes

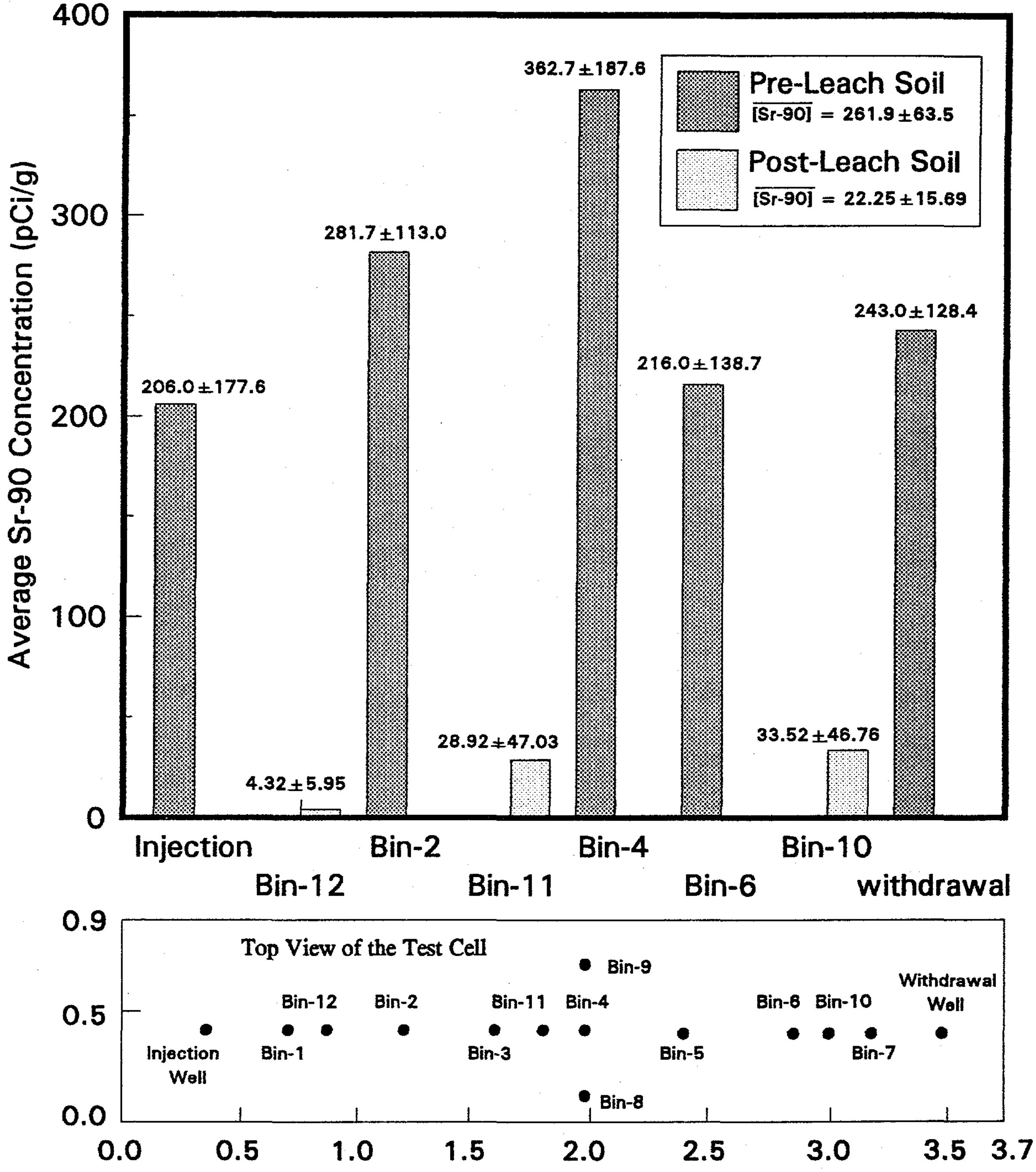


Figure A.34: Average Sr-90 Concentrations in Pre-Leaching and Post-Leaching Soils

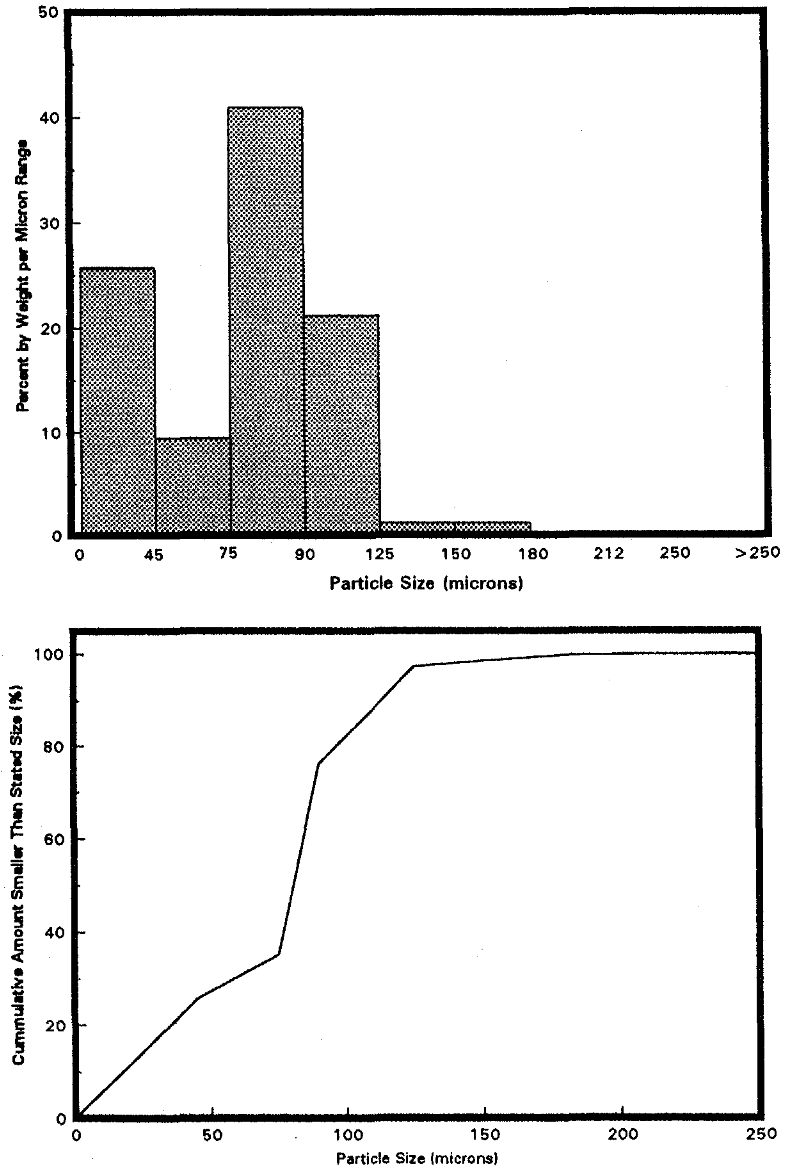


Figure A.35: Particle-Size Distribution for Chalk River Chemical Pit Soil Employed in Pilot-scale Ex-situ Soil Leaching Study (Ground)

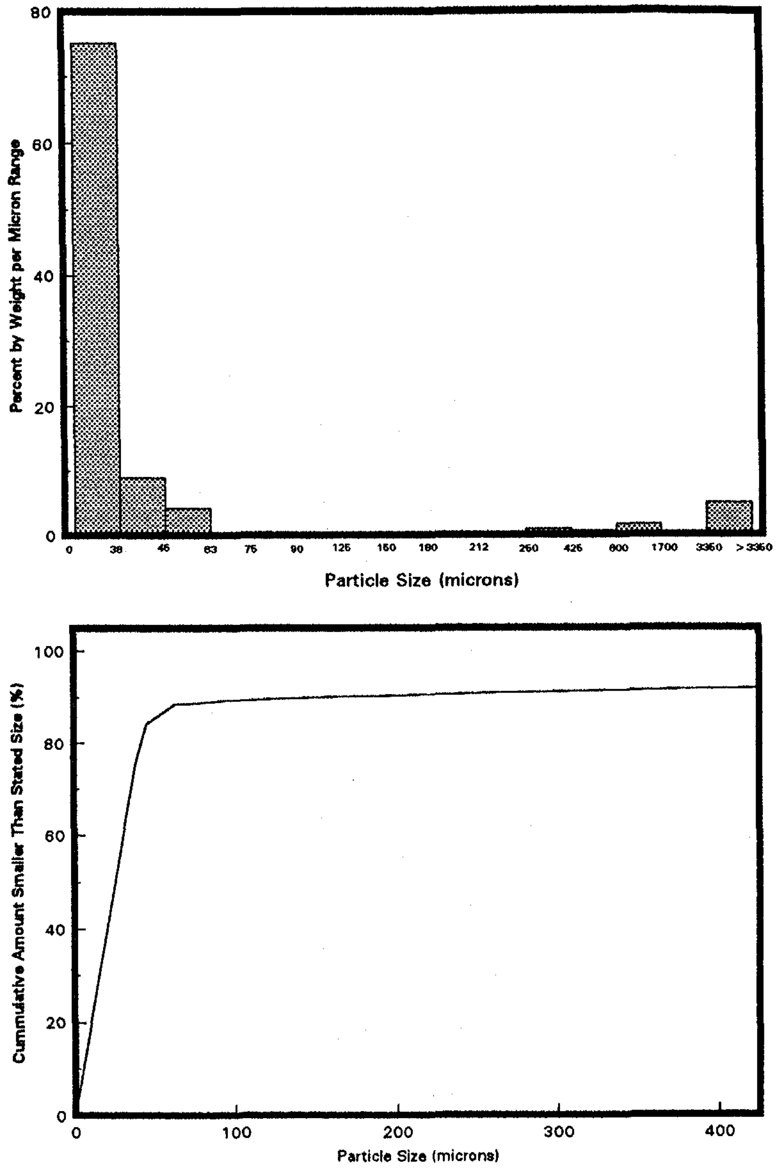
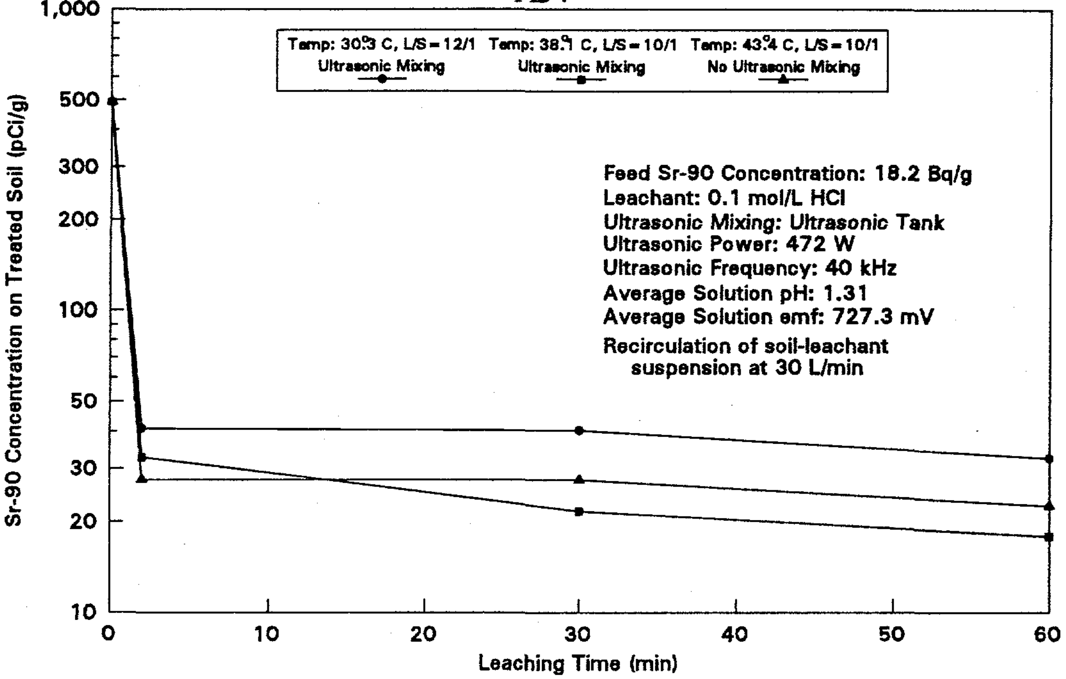
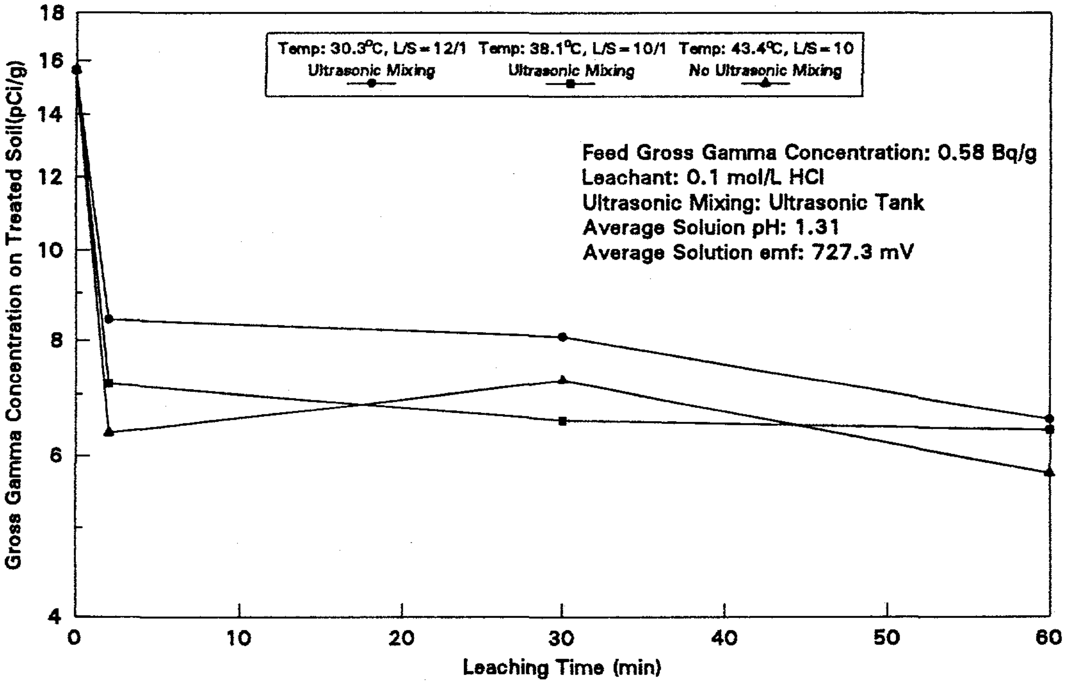


Figure A.36: Particle-Size Distribution for Fernald Incinerator Area Soil Employed in Pilot-scale Ex-situ Soil Leaching Study (As Received)



Feed Sr-90 Concentration: 18.2 Bq/g
Leachant: 0.1 mol/L HCl
Ultrasonic Mixing: Ultrasonic Tank
Ultrasonic Power: 472 W
Ultrasonic Frequency: 40 kHz
Average Solution pH: 1.31
Average Solution emf: 727.3 mV
Recirculation of soil-leachant suspension at 30 L/min

Figure A.37: Residual Strontium-90 Concentration in the Chalk River soil using a Soil Suspension Flow Rate of 30 L/min with and without an Ultrasonic Field as a Function of Leaching Time
(See Figure A.8 for Experimental Arrangement)



Feed Gross Gamma Concentration: 0.58 Bq/g
Leachant: 0.1 mol/L HCl
Ultrasonic Mixing: Ultrasonic Tank
Average Soluion pH: 1.31
Average Solution emf: 727.3 mV

Figure A.38: Residual Gross Gamma Concentration in the Treated Chalk River Soil as a Function of Leaching Time

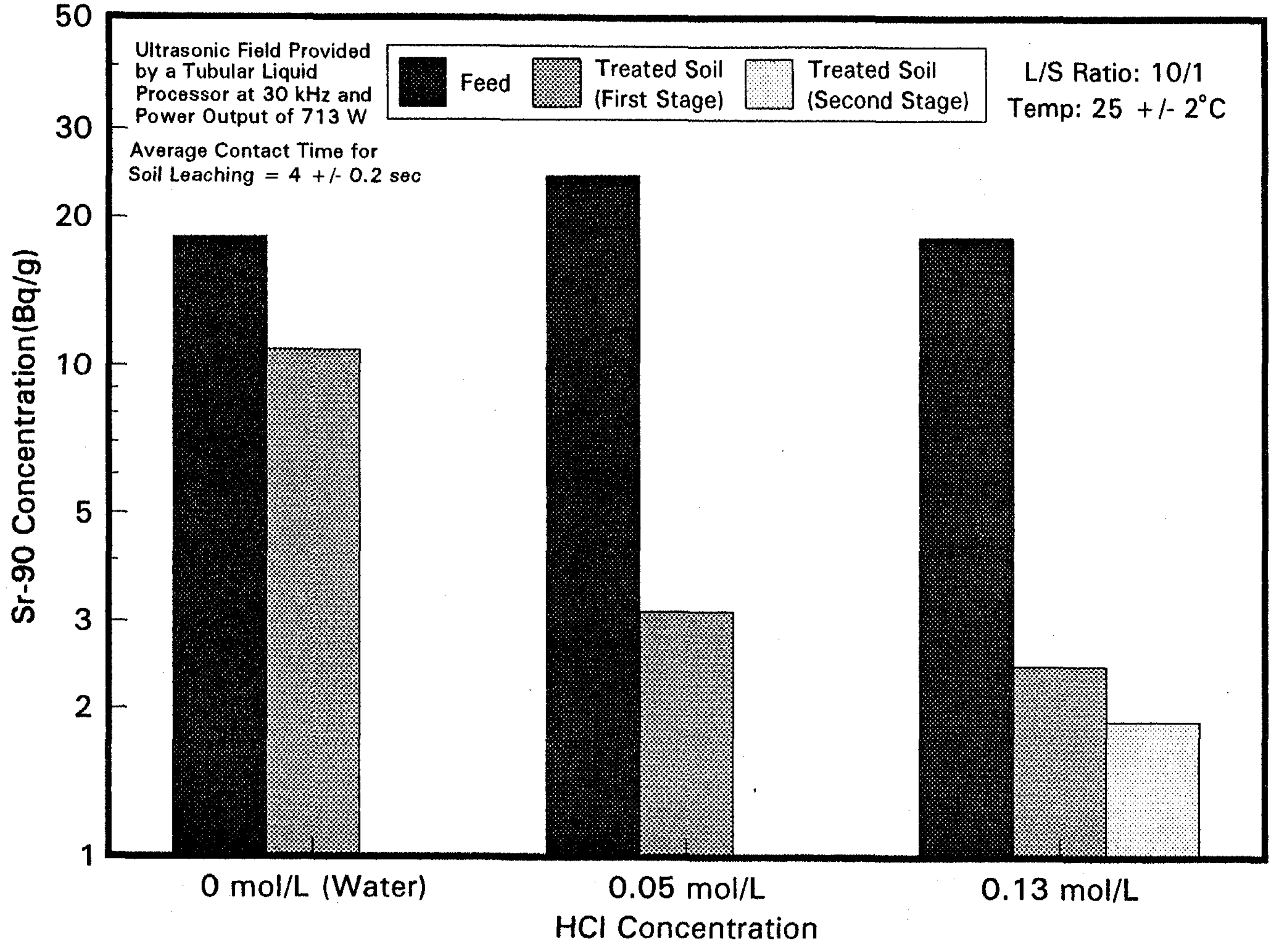


Figure A.39: Effect of Leachant Concentration on Sr-90 Removal Efficiency for Chalk River Soil using a Tubular Ultrasonic Processor (Contact Volume: 0.65 L) at a Soil-Water Suspension Feed Rate of 10 L/min [See Figure A.9 for Experimental Arrangement]

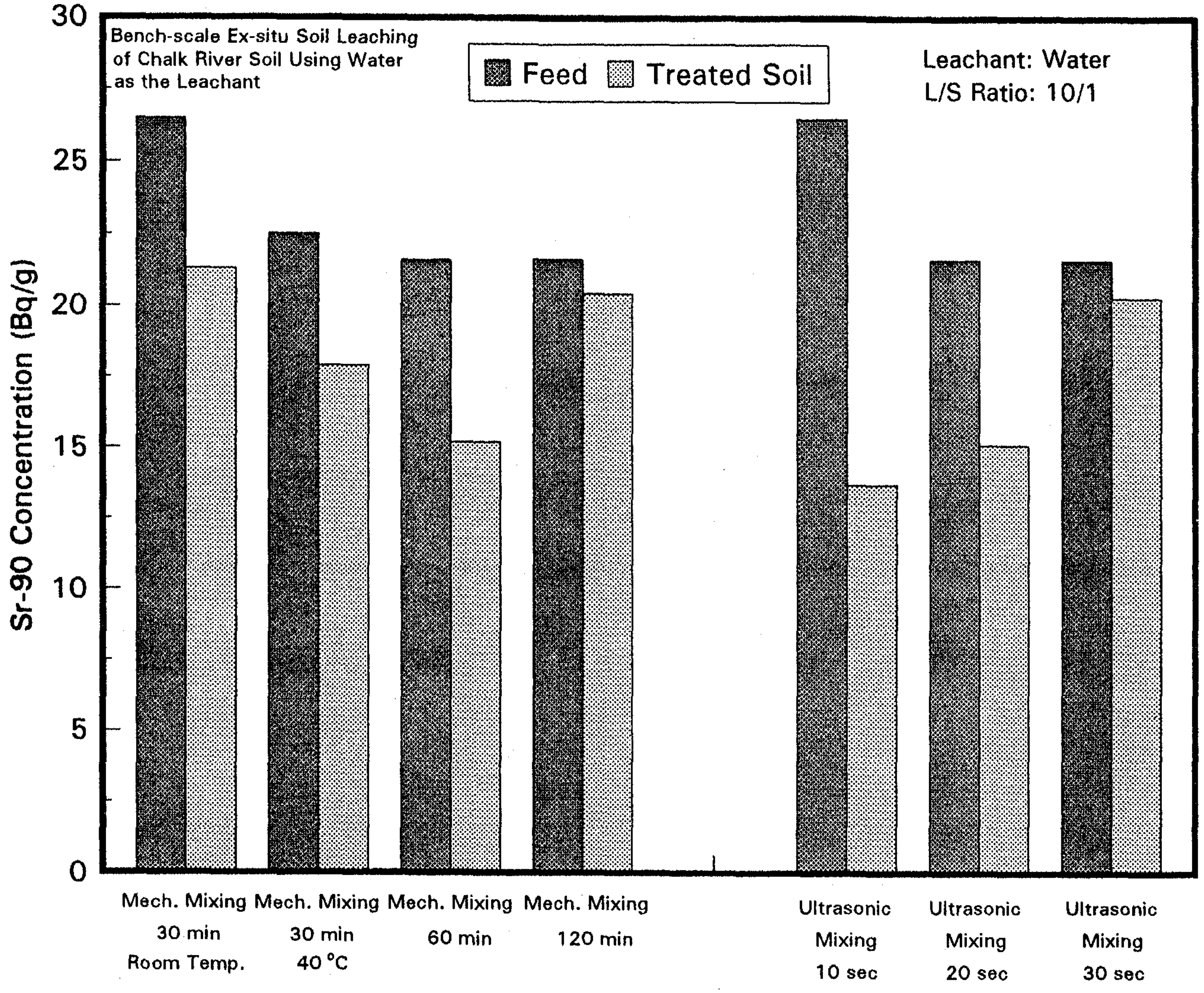
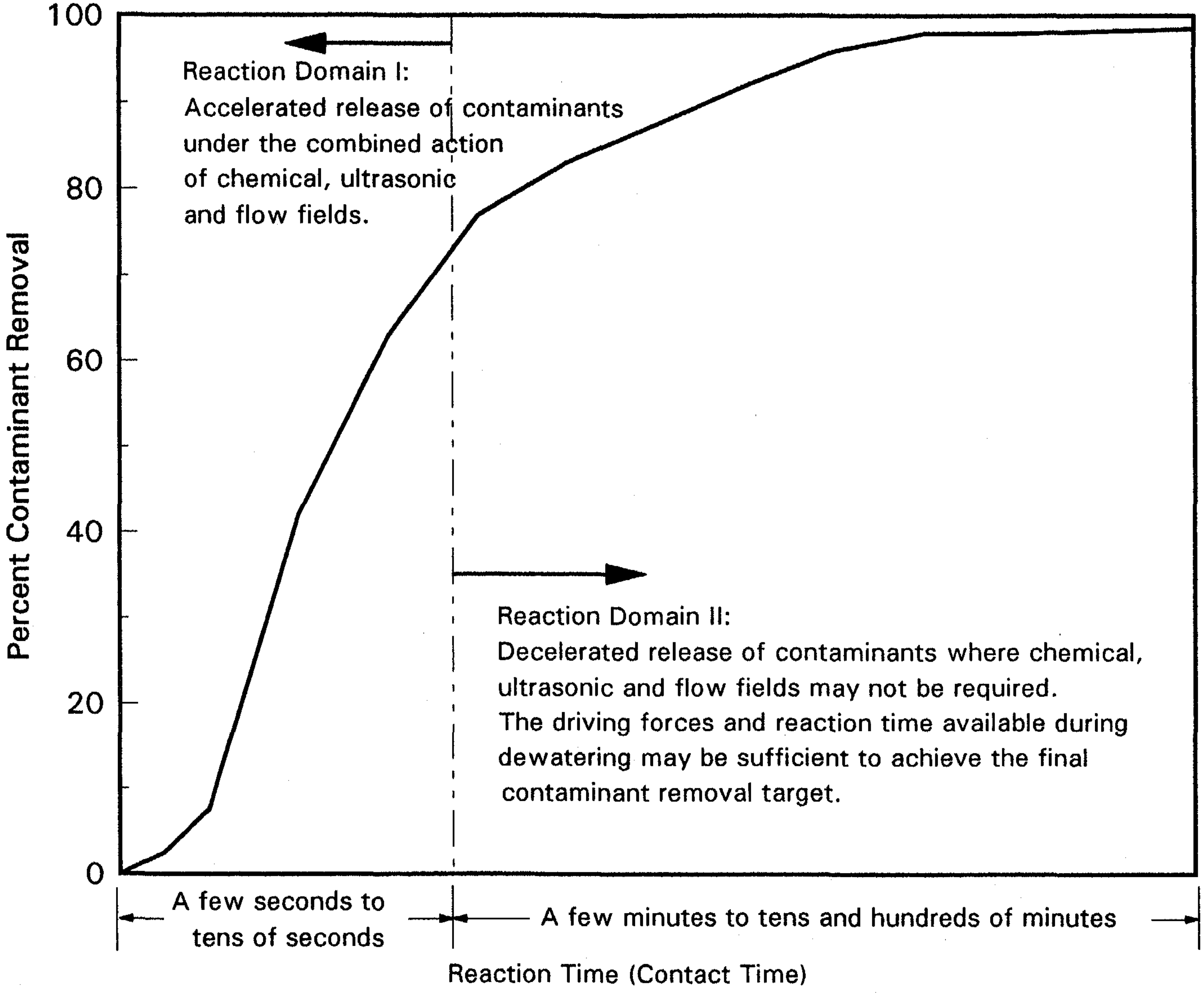


Figure A.40: Effects of Type of Mixing and Leaching Time on Sr-90 Removal by Bench-Scale Water Leaching of Chalk River Soil at Room Temperature (23-25°C)



Reaction Domain I:
Accelerated release of contaminants
under the combined action
of chemical, ultrasonic
and flow fields.

Reaction Domain II:
Decelerated release of contaminants where chemical,
ultrasonic and flow fields may not be required.
The driving forces and reaction time available during
dewatering may be sufficient to achieve the final
contaminant removal target.

Figure A.41: A Conceptual Diagram for Soil Leaching Kinetics

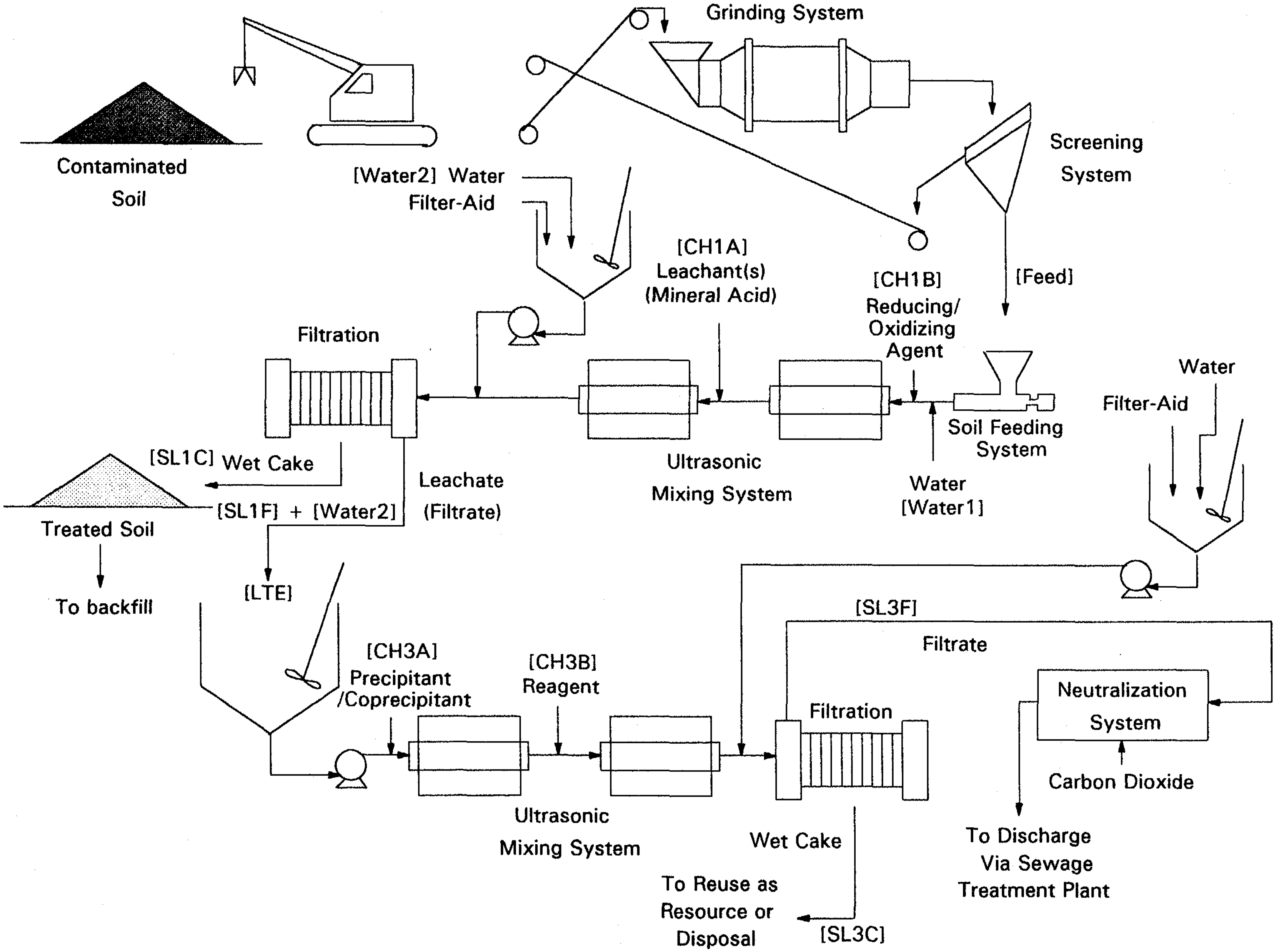


Figure A.42: Proposed Process Flowsheet for Ex-Situ Soil Decontamination and Leachate Treatment

APPENDIX B

TABLES SUMMARIZING EXPERIMENTAL AND ANALYSIS DATA

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF TABLES (continued)

LIST OF TABLES (continued)

Table B.1: A Summary of Primary Equipment Used in Bench-Scale Tests

Equipment	Description
Primary Equipment:	
Flotation	Laboratory-scale Denver Flotation Machine, Model D12
Ultrasonic-Aided Soil Leaching	Leaching Vessel: 250 to 1 liter pyrex glass beaker Ultrasonic System 1: Branson 184V, Serial No. KQ6011A generator equipped with 1 inch titatnium horn with silver booster; Power: 960 watts ; Frequency:20 kHz Ultrasonic System 2: Fisher Sonic Dismembrator, Model 300, 3/4 inch titanium horn Serial No. A515852; Power: 300 watts; Frequency:21 kHz.
Mechanical Leaching	Leaching Vessel: 250 to 1 liter pyrex glass beaker Fisher Dynamics Model 143 agitator/controller system equipped with 2 inch diameter impeller; rpm: 600 Power:18 to 20 watts.
Solid-Liquid Separation	
Buchner Filtration	Standard vacuum filtration flasks (1 to 2 liters), fitted with porcelain and polyethylene Buchner funnels and Whatmann #3 filter paper.
Microfiltration	Amicon Model 8400 apparatus with 400 mL filtration vessel and fitted with 3 inch diameter polypropylene filter (0.2 μm pore diameter) from Memtec America Corp.
Toxicity Characteristic Leaching Procedure (TCLP)	Sample mixer Serial No. 1096 from Associated Design and Manufacturing Company, equipped with 2-liter teflon bottles; filtration of leach solution performed using a Gelman Scientific filtration system fitted with 0.4μm filter, Product No. 11872, Serial No. P1043

Table B.2: A Summary of Ancillary Equipment and Instruments Used in Bench-Scale Tests

Equipment	Description
<u>**Ancillary Equipment:**</u>	
Magnetic Stirring	Fisher Scientific Thermix stirrer Model 120 MR, Serial No. 81001435, teflon coated stirrer bars 1/2 inch to 3 inch diameter
Soil Grinder	US Stoneware Roller Serial No. CZ-92252
Soil Grinding Jar	Roalox Burundum-Fortified Grinding Jar (from Fisher Scientific), 0.3 and 1.3 gallon capacity, with burundum cylindrical grinding media and zirconia grinding media
Soil Drying	Fisher Isotemp oven Model 175, Serial No. 146
Dried Soil Grinder	Moulinex coffee grinder
Soil Sieving and Particle-size Determination	W.S. Tyler stainless-steel Standard Sieves 40 to 400 (from W.S. Tyler Canada); Sepor, Inc. Wet/Dry Sieve Shaker, Cat. No. 040B-001; also, Thomas Scientific Sieve Shaker Serial No. BB80825 11 90
<u>**Measurement/Control Instrument:**</u>	
Solution pH	Accumet pH/emf meter 915, Fisher Scientific Serial No. 5531, equipped with combination electrode with Ag/AgCl (4M KCl) reference electrode, temperature probe, Catalogue No. 13-620-16
Solution e.m.f.	Accumet pH/emf meter 915, Fisher Scientific Serial No. 3132, equipped with an Orion emf electrode, Catalogue No.97-78-00 and a temperature probe (Cat. No. 13-620-16)
Constant Temperature Bath	Cole Parmer Poystat Model 1253-00 consisting of a Circulator (Serial No. 8995-2804) and a Techne Bath
Temperature	Omega Model HH21 microprocessor fitted with a J thermocouple (Serial No. T-97111)
Current Meter	Fluke 8010A digital multimeter
Time	Digital stop watch from Fisher
Agitator rpm	Cole Parmer digital tachometer, Model 08212

Table B.3: Summary of Primary Equipment and Instruments Used in Pilot-scale Ex-situ Soil Leaching and Leachate Treatment Study

Equipment/Function	Description
Ultrasonic tank	Branson Ultrasonic Corp., Power generator model S8040-18; 38 liter volume Ultrasonic tank, model CH-1216-40-18, equipped with eighteen 40 kHz transducers and temperature control system using Type K thermocouple.
Ultrasonic (tubular) liquid processor	Branson Ultrasonic Corp., model LP3-16 with a cylindrical (0.07-m dia x 0.2-m long) 30 kHz transdurized process chamber; power supplied by the generator model EMW-50-16
Frame and plate filterpress	Perrin, manual-hydraulically driven model 100-18 with 7 plates and a total filter area of 4.14 m^2; polypropylene filter cloth with a 3 cfm porosity rating
Cross-flow microfiltration	Memtech America, Memcor Micro Compact Unit, equipped with 2 m^2 surface area polypropylene hollowfiber membranes (0.2 μm pore dia.)
Tubular filter press	EPOC Water Inc., EXXPRESS STP system
Mechanical mixer	Lightnin, model V5P18
Electrical water heater	Process Technology, Model 5235, 500 W st. steel
Temperature control system	AECL design fitted with Type J thermocouple
Soil slurry delivery pump	Sand Piper, double-diaphragm, model SB1-A Type 4
Leachate delivery pump	Continental CP-56-SSBMT progressive cavity pump
Reagent metering pumps	Liquid, Metionics Inc., model A 761-61S
Solution pH control system	Cole Parmer, flat surfaced pH electrode, model G-27003-40, with G-05821-00 controller
Oxidation Reduction Potential (ORP) measurement system	Cole Parmer, flat-surfaced ORP electrode, model G-27003-40, with G-05821-00 controller
Batch pressure filtration	Minpro Ltd., fitted with Whatman 541 filter paper system (25 μm di. particle retention rating)
Feed, Holding and Collection tanks	1000 litre polypropylene conical bottom tanks

Table B.4: Chemical Reagents Employed in the Study

Chemical	Description	Used As
Acetic acid - glacial CH_3COOH	ACS Grade, Fisher Scientific Lot# 509423	Leachant
Air	Liquid Air; Purity: 99 %	Oxidant
Ammonium bicarbonate NH_4HCO_3	Certified, Lot# 935788 Fisher Scientific	Leachant/buffer
AWA-1380, Complexant	Albright & Wilson Americas	Leachant/collector
Calcium carbonate $CaCO_3$	Certified ACS, Lot# 930511 Fisher Scientific	Precipitant
Calcium hydroxide $Ca(OH)_2$	Certified, Fisher Scientific Lot# 916636A	Precipitant/pH modifier
Carbon dioxide (CO_2)	Matheson Gas Product Canada, Lot# P31-1814-4	Precipitant/ Neutralizer
Chabazite	Natural Zeolite (TZS-500H) Fisher Technical Development, Inc.	Sorbent
Citric acid anhydrous $HO_2CCH_2C(OH)(CO_2H).CH_2CO_2H$	ACS Certified, Fisher Scientific, Lot# 904847A	Leachant
Clinoptilolite	Natural Zeolite (TSM-140H) Steelhead Speciality Minerals	Sorbent
Cupferron Ammonium N-nitro-phenyl-hydroxylamine	BDH Chemicals, Lot# 54369, analar, F.W. 155.16 Pfaltz & Bauer, Inc., ID# C27130	Flotation collector
Cyanex 925 extractant bis(2,4,4,-trimethy-pentyl)octylphosphene oxide	Developmental reagent, Highly hindered phosphene oxide Cyanamid Canada Inc.	Flotation Collector
Ferric chloride hexahydrate	Anachemia, Lot# 390104 Assay 97-102%	Oxidant
Ferric sulphate, n-hydrate $Fe_2(SO_4)_3.nH_2O$	J.T. Baker Chemical Co., Lot# 9486893	Oxidant
Harborlite	Harborlite 800S	Filter-aid

Table B.4 (continued)

Chemical	Description	Used As
Hydrochloric acid	Anachemia, Lot# 292329 Assay: 36.5-38.0%; Sp.Gr. 1.18	Leachant
Hydrogen Peroxide(H_2O_2)	ACS Grade, Lot# 390316, 30% soln.	Precipitant
Ionquest 201 (an alkyl phosphonic acid)	Albright & Wilson Americas Lot# 07093SILU1002355DR, MW. 206	Leachant/Flotation collector
Magnesium hydroxide $Mg(OH)_2$	Fisher Scientific, Lot# 720847	Precipitant/pH modifier
Nitric acid (HNO_3)	Anachemia, Lot# 392329, 69-71%	Leachant
Potassium permanganate $KMnO_4$	ACS Grade, Anachemia	Oxidant
Potassium persulphate $K_2S_2O_8$	Allied Chemical assay: min. 98%	Oxidant
Redox Standard Solution Ferrous-Ferric Reference Soln.	ASTM Standard D1498-76 (reapproved 1981)	Calibrating ORP Response Electrode
Sodium bicarbonate $NaHCO_3$	Anachemia, Lot# 390202 ACS Certified	Leachant/buffer
Sodium carbonate Na_2CO_3	Fisher Scientific, Lot# 884559	Leachant/ Precipitant
Sodium Citrate $Na_3C_6H_5O_7.2H_2O$	B&A, Analar	Leachant
Sodium fluoride NaF	Certified, Fisher Scientific Lot# 783787	Modifier in leaching
Sodium hypochlorite NaOCl	Purified Grade, Lot# 936482-9 Fisher Scientific	Oxidant
Sodium hydroxide NaOH	Anachemia, ACS Grade, Lot# 680808	pH modifier/ precipitant
Sodium dithionite	Anachemia, Lot# 07223	Reductant
Sodium silicate `N'	Sample, Sp.Gr. 1.394 (liq.) Na_2O (8.90%), SiO_2 (28.7%) National Silicates	Depressant in Flotation

Table B.4 (continued)

Chemical	Description	Used As
Sulphuric acid H_2SO_4	ACS Certified, Anachemia Lot# 198970, assay: 95-98%	Leachant
Tiron $(HO)_2C_6H_2(SO_3Na)_2.H_2O$	Aldrich Chemical Co.Lot# 0223NZ 4,5-dihydroxy-1,3-benzenedi-sulphonic acid, disodium salt monohydrate	Flotation collector

Table B.5: Analysis of Untreated Fernald Incinerator Area Soil

Serial #	Sample Code	[U] (DNC) ug/g	[U] (ICP) ug/g	[Al] (ICP) ug/g	[Ca] (ICP) ug/g	[Fe] (ICP) ug/g	[Mn] (ICP) ug/g	[Pb] (ICP) ug/g	FSQI (DNC)
(a) Bench-scale Ex-situ Soil Leaching Tests									
1	SLI	555	-	-	-	-	-	-	10.7
2	SLI	498	-	-	-	-	-	-	9.6
3	SLI	528	-	-	-	-	-	-	10.2
4	SLI1	-	558	13200	10100	21300	830	38.7	-
5	SLI1	552	-	-	-	-	-	-	10.6
6	SLI1	552	-	-	-	-	-	-	10.6
7	SLI2	597	-	-	-	-	-	-	11.5
8	SLI2	-	588	13700	9890	22000	952	35.1	-
9	SLI2	-	585	14100	20000	21450	928	34.2	-
10	SLI2	538	-	-	-	-	-	-	10.3
11	SLI2	-	595	12900	8540	21200	941	35.9	-
12	SLI2	-	603	12700	8950	21600	950	36.3	-
13	SLI2	558	-	-	-	-	-	-	10.7
14	SLI2	548	-	-	-	-	-	-	10.5
15	SLI2	570	-	-	-	-	-	-	11.0
16	SLI2	594	-	-	-	-	-	-	11.4
17	SLI2	523	-	-	-	-	-	-	10.1
18	SLI2	547	-	-	-	-	-	-	10.5
122	SLI2	601	-	-	-	-	-	-	11.6
123	SLI2	594	-	-	-	-	-	-	11.4
124	SLI2	596	-	-	-	-	-	-	11.5
125	SLI2	606	-	-	-	-	-	-	11.7
126	SLI4	568	-	-	-	-	-	-	10.9
127	SLI4	556	-	-	-	-	-	-	10.7
128	SLI4	566	-	-	-	-	-	-	10.9
129	SLI4	567	-	-	-	-	-	-	10.9
Overall Average		563	586	13300	11500	21500	920	36.0	10.8
Standard Deviation, s		28	17	576	4800	313	51	1.7	0.5
(b) Pilot-scale Ex-situ Soil Leaching Tests (Dry Soil Feed)									
1	As received	472							9.1
2	As received	485							9.3
3	As received	493							9.5
4	As received	488							9.4
5	As received	706							13.6
6	As received	571							11.0
7	As received	580							11.2
8	As received	605							11.6
9	As received	532							10.2
Overall Average		548							10.5
Standard Deviation, s		76							1.5
(c) Pilot-scale Ex-situ Soil Leaching Tests (Soil Sieved with Water)									
T1	As received	532							10.2
T2	As received	594							11.4
T3	As received	664							12.8
T4	As received	672							12.9
Overall Average		615							11.8
Standard Deviation, s		66							1.3

Note: SLI - unground Fernald IA Soil
SLI1 - batch #1 ground Fernald IA Soil
SLI2 - batch #2 ground Fernald IA Soil
SLI4 - ground Fernald IA Soil
FSQI - Feed Soil Quality Index = ([U] / 52)
'-' Not Measured

Table B.6: Analysis of Untreated Chalk River Chemical Pit Soil

Serial #	Activity (pCi/g)				Metal Concentration ($\mu g/g$)			FSQI		
	Sr-90	Co-60	Cs-137	Gross Gamma	Ca	Fe	U	Sr-90	Gross Gamma	Total Activity
(a) Bench-scale Ex-situ Soil Leaching Tests										
1	1134.00	64.80	1.67	66.47	-	-	-	32.40	1.90	34.30
2	899.10	73.71	< 1.08	74.79	1685	5310	4.25	25.69	2.14	27.83
3	912.60	75.33	1.39	76.72	1450	5500	3.80	26.07	2.19	28.27
4	1347.30	86.40	< 1.35	87.75	1490	5920	6.80	38.49	2.51	41.00
5	1379.70	71.55	< 1.35	72.90	1910	5920	7.10	39.42	2.08	41.50
6	1382.40	90.72	< 1.35	92.07	1520	5380	7.20	39.50	2.63	42.13
7	1336.50	90.72	< 1.35	92.07	1835	5765	7.90	38.19	2.63	40.82
8	896.40	50.49	< 1.08	51.57	-	-	-	25.61	1.47	27.08
9	904.50	48.60	< 1.08	49.68	-	-	-	25.84	1.42	27.26
10	1487.70	93.42	< 1.62	95.04	3130	8650	7.50	42.51	2.72	45.22
11	1525.50	95.85	2.94	98.79	3130	8620	8.00	43.59	2.82	46.41
12	1169.10	59.40	3.29	62.69	-	-	-	33.40	1.79	35.19
13	1285.20	61.02	2.75	63.77	-	-	-	36.72	1.82	38.54
81	1024	118.97	< 0.81	119.78	-	-	-	29.27	3.42	32.69
82	1046	123.58	< 0.81	124.39	-	-	-	29.89	3.55	33.44
83	1057	128.18	< 1.36	129.54	-	-	-	30.20	3.70	33.90
84	991.9	119.51	< 0.81	120.32	-	-	-	28.34	3.44	31.78
Overall Average	1204.62	74.00	1.72	75.72	2019	6383	6.57	34.42	2.16	36.58
Standard Deviation, s	234.44	16.43	0.76	16.47	660	1409	1.62	6.70	0.47	7.06
(b) Soil Column Leaching Tests										
Soil Columns B,C&D	216.30	15.50	0.84	18.40	-	-	-	6.18	0.53	6.71
Standard Deviation, s	54.00	1.90								
(c) In-situ Soil Leaching Tests										
	260.00	7.30	-	-	-	-	-	7.43	0.21	7.64
(d) Pilot-scale Ex-situ Soil Leaching Tests										
P1	491.00	11.70	< 0.42	15.60				14.06	0.45	14.48
P2	532.00	11.00	1.46	16.00				15.20	0.31	15.51
Overall Average	512.00	11.40	1.46	15.80				14.63	0.45	15.08
Standard Deviation, s	36.30	0.62		0.36						

Note: A target guideline for Treated Soil of 35 pCi/g is assigned
Ru-106 value is less than delection limit, ie. 10-15 pCi/g, depending on the sample matrix
Gross gamma = Co-60 + Cs-137
SLI1 - Soil core sample no. ES-16
SLI2 - Soil core sample no. CP-4
SLI3 - Soil core sample no. CP-4, ground to - 200 mesh
FSQI - Feed Soil Quality Index = ([Sr-90]/35 or [Gross gamma]/35 or [Total Activity]/35)
Total Activity = [Sr-90] + [Gross gamma]

Table B.7: Chemical and Radiochemical Analysis Methods and Sample Detection Limits

Sample Type	Species Analysed	Method Title	Method Type	SDL
Soil, Leachate and Treated Leachate (Bench-scale and Pilot-scale Ex-situ Soil and Leachate Treatment)	Al	Metals by ICP	ICPS Digestion	0.1 mg/L
	Ca			0.1 mg/L
	Fe			0.01 mg/L
	Mn			0.005 mg/L
	Mg			0.005 mg/L
	Pb			0.8 mg/L
	U			0.5 mg/L
	U	Uranium by Scintrex	Laser Fluorescence	0.5 µg/L
	U	Uranium by Delayed Neutron at $5x10^{11}$ cm^2/s neutron		Absolute DL is 0.1 µg U-238
Soil Leachate and Treated Leachate	SO_4	Anions by IC	IC	
	TDS	Total Dissolved Solids	Filtration/ Gravimetric	0.5 mg/L 1.0 mg/L
Soil (Bench-scale and Pilot-scale Ex-situ)	^{90}Sr	Liquid Scintillation Counting	Microwave/HNO_3 Digestion	0.6 Bq/g (2 g sample) 0.24 Bq/g (5 g sample)
	^{60}Co	Gamma Spectrometry	Marinelli Beaker Well Detector	2 - 8 Bq/kg 30 Bq/kg
	^{137}Cs		Marinelli Beaker Well Detector	1 - 5 Bq/kg 20 Bq/kg
Soil (Soil Column and In-situ Soil Leaching)	^{90}Sr	Beta Counting of sample mounted on st. steel Planchets	Counting by Gas Flow Proportional Counter Fitted with Guard Detectors	0.59 Bq/g
	^{60}Co	Gamma Scanning	By NaI Counter	0.07 Bq/g

Table B.7 (continued)

Sample Type	Species Analysed	Method Title	Method Type	SDL
Leachate and Treated Leachate (Bench-scale and Pilot-scale Ex-situ)	^{90}Sr	Scintillation Equilibrium for 21 Days	After ^{90}Sr/^{90}Y	20 Bq/L
	^{90}Sr	Scintillation Counting	After ^{90}Y Separation	1 Bq/L
Leachate (Soil Column and In-situ Leaching)	^{90}Sr	Cherenkov Beta Analysis	By Liquid Scintillation Counting	30 Bq/L
	^{60}Co	Gamma Counting		3 Bq/L

Notes:

SDL: Sample Detection Limit
TDS: Total Dissolved Solids
DL: Detection Limit
IC: Ion Chromatography

Table B.8: Summary of Chemical Analysis Experimental Errors

Species	Concentration Range (mg/kg)	Average 2s%	Species	Concentration Range (mg/kg)	Average 2s%
Fernald Incinerator Area Soil			Chalk River Chemical Pit Soil		
Soil Feed			Soil Feed		
Al	12 000 - 14 000	2.5	Ca	1 500 - 2 000	0.8
Ca	9 000 - 20 000	2.3	Ca	3 000	2.3
Fe	21 000 - 22 000	2.7	Fe	4 000 - 9 000	2.4
Mn	830 - 850	1.7	U	4 - 8	10
Pb	30 - 40	4.5	^{90}Sr	900 - 1500	10
U	550 - 600	4.0	^{60}Co	60 -100	10
			^{137}Cs	1 - 2	50
			^{137}Cs	2.7 - 4.6	30
			Gross γ	50 - 100	10
H_2SO_4 Treated Soil			HCl Treated Soil		
Al	480 - 6 800	1.2	^{90}Sr	50 - 100	20
Al	9 000 - 13 000	2.5	^{90}Sr	30 - 60	8
Ca	200 - 8 000	1.2-2.2	^{60}Co	5 - 25	10
Fe	116 - 20 000	3.0	^{137}Cs	2 - 4	33
Mn	60 - 664	2.3	Gross γ	7 - 30	10
Pb	20 - 30	9.0			
U	30 - 200	4.0			
Soil Leachate Feed				Soil Leachate Feed	
Al	200	1.5	Ca	95-115	1.7
Ca	750	7	Fe	190-256	3.3
Fe	200 - 500	6.3	U	< 0.5	10
Mn	260	1.5	U	2.7	4
Pb	< 0.8	2.6	^{90}Sr	120 000 - 130 000	20
SO_4	20 000 - 27 000	5.0	^{60}Co	3 000 - 7 000	20
TDS	24 000 - 34 000	3.0	^{137}Cs	160 - 270	100
			Gross γ	1 000 - 1 300	20
			TDS	3 000 - 40 000	3
Treated Leachate			Treated Leachate		
Al	0.1 - 100	1.5	Ca	3 - 7	3.2
Ca	600 - 800	7.0	Fe	0.05 - 0.3	14
Fe	0.1 - 0.3	2.3	U	0.1 - 0.2	10
Fe	0.03 - 0.1	6.3	^{90}Sr	100 - 380	48
Mn	0.02 - 160	1.5	^{60}Co	540 - 800	20
Pb	< 0.8	2.6	TDS	2 500 - 25 000	3
U(ICP)	0.6 - 10	6.0			
U(Scintrex)	0.11	10.0			
SO_4	1 700 - 2 200	5.0			
TDS	2 600 - 3 600	3.0			

Table B.9: Summary of Other Experimental Errors

	Bench-scale Tests			Pilot-scale Tests		
	Total Error % 2s	Analytical Error % 2s	Experimental Error % 2s	Total Error % 2s	Analytical Error % 2s	Experimental Error % 2s
Residue Weight:						
Fernald Soil	10	0.2	10			
CRL Soil	2	0.2	2			
Feed Assay:						
Uranium	9	4	8	27	4	27
Sr-90	25	8	24	14	8	11
Gross Gamma	50	12	9	5	12	--
Residue Assay:						
Uranium	10	4	9	7.3	1.8	7.1
Sr-90	9	8	4			
Gross Gamma	15	12	9			
% Soil Dissolved:						
Fernald Soil	13	0.2	13			
CRL Soil	2	0.2	2	7.5	0.2	7.5

Note :1) Total error in PCRE is ~14% (2s%) for all contaminants in the two soils in bench-scale tests
2) Total error in PCRE is 4% for uranium in pilot-scale tests

Table B.10: Bench-scale Soil Flotation Conditions and Results

Fernald Incinerator Area Soil

TEST CONDITIONS						CONCENTRATION	CALCULATED RESULTS		
Serial #	Stream	Mass g	Reducing Agent	Collector g/100 g soil	pH	[U] µg/g	Amount of U µg	U Dist'n %	Mass Loss % Soil
19	Feed	100.00	Nil	-	-	559	55900	100.00	-
20	Tails	56.15	Nil	1 g	Natural	458	25717	46.00	-
	Float	38.62		Cupferron	pH	595	22979	41.11	5.23
21	Tails	70.19	Nil	0.5 mL	7.5	457	32077	57.38	-
	Float	21.94		Ion Quest 201		601	13186	23.59	7.87
22	Tails	76.80	Nil	1 mL	7.5	482	37018	66.22	-
	Float	17.51		Ion Quest 201		N/A	N/A	33.78	5.69
23	Tails	71.89	Nil	1 g	7.5	450	32351	57.87	-
	Float	22.78		Tiron		N/A	N/A	42.13	5.33
24	Tails	64.49	Nil	2 drops	Natural	630	40629	72.68	-
	Float	31.12		Cyanex 302	pH	N/A	N/A	27.32	4.39
25	Tails	76.29	Nil	2 drops	Natural	532	40586	72.61	-
	Float	19.02		Cyanex 925	pH	N/A	N/A	27.39	4.69
26	Tails	54.22	Nil	2 g	Natural	461	24995	44.71	-
	Float	39.74		Cupferron	pH	N/A	N/A	55.29	6.04
27	Tails	75.62	Nil	2 mL Ion Quest 201	Natural	416	31458	56.28	-
	Float	19.40		& 30 mg AWA-1380	pH	N/A	N/A	43.72	4.98
28	Tails	61.93	3.88 g Na2S2O4	1 g	Natural	503	31151	55.73	-
	Float	33.32	to emf - 580 mV	Cupferron	pH	703	23424	41.90	4.75
29	Tails	67.40	2 g Na2S2O4	1 g	7.5	511	34441	61.61	-
	Float	24.81	to emf - 580 mV	Tiron		N/A	N/A	38.39	7.79
30	Tails	54.14	Nil	5 g Cupferron &	Natural	294	15917	28.47	-
	Float	41.52		1 mL Na2•SiO2 "N"	pH	N/A	N/A	71.53	4.34
31	Tails	75.39	2 g Na2S2O4	1 g Cupferron &	Natural	521	39278	70.27	-
	Float	19.36	to emf - 580 mV	2 drops Bunker C Oil	pH	N/A	N/A	29.73	5.25

Chalk River Chemical Pit Soil

Serial #	Stream	Mass g	Reducing Agent	Collector g/100 g soil	pH	Activity (pCi/g)		[U] µg/g	Amount (pCi)		Distribution %		U Dist'n %
						Sr-90	Gross Gamma		Sr-90	Gross Gamma	Sr-90	Gross Gamma	
14	Feed	100.05	Nil	-	-	1366.88	80.08	7.8	136756	8012	100	100	100
15	Tails	49.12	Nil	4 g	Natural	1309.50	78.30	5.0	64323	3846	47.03	48.00	31.67
	Float	44.91	Nil	Cupferron	pH	N/A	N/A	N/A	N/A	N/A	52.97	52.00	68.33

Note: N/A - Sample was not analyzed
Gross gamma = Co-60 + Cs-137
Frother - Aerofroth 65

Table B.11: Calculated Flotation Yield Required to Achieve 35 pCi U/g (52 µg/g) of Residue

Scenario	Stream	Weight (g)	Uranium Conc. (µg/g)	Amount of Uranium (µg)	Uranium Distribution (%)	DF	VRF
	Soil Feed	100	559	55 900	100		
I (minimum acceptable target)	Tail	50	52	2 600	5	10.8	2
	Float	50	1066	53 300	95		
II (desired target)	Tail	80	52	4 160	7	10.8	5
	Float	20	2627	51 740	93		
Our Best Results	Tail	54	294	15 917	29	1.9	2.4
	Float	42	962	39 942	72		

Table B.12 : Fernald Incinerator Area Soil Leaching - Experimental Conditions and Uranium Removal Results

TEST CONDITIONS / MEASURED QUANTITIES																CONCENTRATION	CALCULATED RESULTS		
Serial #	Leachant	Leachant Concentration (mol/L)	Redox Agent	Redox Agent Concentration (g/g soil)	Feed Weight g	Residue Weight g	Initial pH	Final pH	Initial emf mV	Adjusted emf mV	Final emf mV	Mixing Method	Leaching Time min.	Mean Temp. °C	Power Input W	[U] (DNC) ug/g	PCRE U %	Soil Dissolved %	TSQI (DNC)
34	H2SO4	0.3	KMnO4	0.001	20.00	19.00	0.7	0.7	692	1010	679	US	3	46	305	83.0	85.7	5.0	1.60
35	H2SO4	0.3	KMnO4	0.001	20.00	18.27	0.7	0.7	628	1039	731	US	6	48	303	97.0	84.0	8.6	1.87
36	H2SO4	0.3	KMnO4	0.001	20.00	17.35	0.7	0.7	656	1031	731	US	9	48	307	91.6	85.6	13.3	1.76
37	H2SO4	0.3	KMnO4	0.001	20.02	18.17	0.7	0.8	663	1047	850	US	3	47	315	91.2	85.0	9.2	1.75
38	H2SO4	0.3	KMnO4	0.002	20.00	18.22	0.9	0.9	688	1086	693	US	3	75	321	70.2	88.4	8.9	1.35
39	H2SO4	0.3	KMnO4	0.0005	20.01	18.39	0.9	0.9	656	1022	765	MECH	15	50	19	88.6	85.3	8.1	1.70
40	H2SO4	0.3	KMnO4	0.0005	20.02	18.18	0.8	0.9	686	1071	706	MECH	45	50	18	80.7	86.7	9.2	1.55
41	H2SO4	0.3	KMnO4	0.0015	20.03	18.00	1.0	1.0	643	1031	615	MECH	90	50	19	59.4	90.3	10.1	1.14
42	H2SO4	0.3	KMnO4	0.001	20.01	18.24	1.0	0.9	657	1061	745	MECH	15	50	20	79.9	86.8	8.8	1.54
43	H2SO4	0.3	KMnO4	0.001	20.02	18.05	0.8	0.9	706	1077	629	MECH	15	75	19	63.6	89.6	9.8	1.22
44	H2SO4	0.3	KMnO4	0.005	75.00	N/A	1.6	1.6	700	1032	854	RECIRC	3	49	276	75.7	86.3	N/A	1.45
45	H2SO4	0.3	KMnO4	0.0035	75.02	N/A	1.5	1.5	675	1050	869	RECIRC	1	48	321	80.5	85.4	N/A	1.55
46	H2SO4	0.1	KMnO4	0.0035	75.01	N/A	1.8	1.8	642	1050	836	RECIRC	3	49	323	104.3	81.1	N/A	2.01
47	H2SO4	0.1	KMnO4	0.003	75.03	N/A	1.7	1.6	658	1051	847	RECIRC	1	45	318	113.3	79.5	N/A	2.18
50	H2SO4	0.1	Air* + Ferric Sulfate	0.5	20.03	18.56	1.5	1.8	514	700	711	US	3	67	340	94.5	84.2	7.3	1.82
51	H2SO4	0.1	Air*	-	20.04	18.52	1.8	1.9	650	-	695	US	3	70	347	110.0	81.6	7.6	2.12
60	H2SO4	0.1	Air*	-	20.08		1.4	1.5	262	-	665	US	3	66	338	-	-	-	-
	H2SO4	0.1	Air*	-		17.22	1.6	1.5	675	-	691	US	3	65	330	64.0	90.5	14.2	1.23
61	H2SO4	0.1	Air* + Ferric Sulfate	0.5	20.00		1.8	1.8	682	725	733	US	3	69	347	-	-	-	-
	H2SO4	0.1	Air* + Ferric Sulfate	0.5		17.36	1.7	1.5	707	751	750	US	3	68	345	61.4	90.8	13.2	1.18
62	H2SO4	0.1	Air*	-	20.03		1.5	1.7	648	-	692	US	3	30	329	-	-	-	-
	H2SO4	0.1	Air*	-		17.60	1.3	1.2	565	-	638	US	3	30	327	90.2	86.3	12.1	1.73
63	H2SO4	0.1	Air* + Ferric Sulfate	0.5	20.00		1.3	1.3	614	660	703	US	3	30	332	-	-	-	-
	H2SO4	0.1	Air* + Ferric Sulfate	0.5		17.09	1.2	1.2	660	690	717	US	3	30	328	80.2	88.1	14.6	1.54
64	H2SO4	0.1	Air* + Ferric Sulfate	0.5	20.06		1.7	1.8	662	712	736	US	3	50	328	-	-	-	-
	H2SO4	0.1	Air* + Ferric Sulfate	0.5		17.60	1.7	1.7	706	738	751	US	3	49	332	70.0	89.4	12.3	1.35
65	H2SO4	0.1	Air*	-	20.04		1.7	1.9	665	-	709	US	3	51	333	-	-	-	-
	H2SO4	0.1	Air*	-		17.99	1.7	1.8	690	-	710	US	3	49	332	78.1	87.9	10.2	1.50
66	H2SO4	0.1	Air*	-	20.04		1.4	1.6	615	-	688	US	3	32	200	-	-	-	-
	H2SO4	0.1	Air*	-		17.87	1.5	1.5	671	-	693	US	3	31	200	91.6	85.9	10.8	1.76
67	H2SO4	0.1	Air*	-	20.00		1.6	1.6	619	-	704	US	6	39	200	-	-	-	-
	H2SO4	0.1	Air*	-		17.81	1.5	1.5	671	-	711	US	6	38	200	76.1	88.3	11.0	1.46
68	H2SO4	0.1	Air*	-	20.04		1.6	1.6	625	-	682	US	1.5	31	401	-	-	-	-
	H2SO4	0.1	Air*	-		17.94	1.4	1.5	670	-	711	US	1.5	37	402	93.6	85.5	10.5	1.80
69	H2SO4	0.1	Air*	-	20.00		1.6	1.7	624	-	699	US	3	36	402	-	-	-	-
	H2SO4	0.1	Air*	-		17.61	1.5	1.5	672	-	698	US	3	36	401	94.9	85.6	11.9	1.83
70	H2SO4	0.1	Air*	-	20.04		1.5	1.8	617	-	679	MECH	33.3	24	18	-	-	-	-
	H2SO4	0.1	Air*	-		17.98	1.8	1.6	678	-	578	MECH	33.3	25	18	91.1	85.9	10.3	1.75
71	H2SO4	0.1	Air*	-	20.02		1.7	1.8	625	-	689	MECH	66.7	25	18	-	-	-	-
	H2SO4	0.1	Air*	-		17.75	1.6	1.7	659	-	684	MECH	66.7	25	18	82.2	87.4	11.3	1.58
72	H2SO4	0.5	KMnO4	0.003	50.03	46.16	0.5	0.5	954	1239	1180	US	3	54	327	65.9	89.5	7.73	1.27
	H2SO4	0.5	KMnO4	0.003	24.88	24.21	0.4	0.4	1204	1288	1290	US	3	52	327	32.3	95.0	10.2	0.62
79	TCLP Extraction Fluid #1	-	-	-	100.01	77.09	4.9	5.3	-	-	-	ROT	1140	25	-	613.0	14.5	22.9	11.79
80	TCLP Extraction Fluid #1	-	-	-	100.03	89.17	4.9	5.3	-	-	-	ROT	1140	25	-	654.0	-0.8	10.9	12.58
81	Na2CO3/ NaHCO3	0.3/ 0.3	-	-	20.00	19.11	9.3	9.3	103	-	90	US	3	50	0	171.0	70.4	4.4	3.29
82	Na2CO3/ NaHCO3	0.1/ 0.1	-	-	20.01	19.27	9.5	9.5	152	-	136	US	3	50	309	224.5	60.9	3.7	4.32
92	Sodium Citrate/ NaHCO3 pH 7.3	0.3	Na2S2O4	0.25	80.00	75.04	8.7	7.0	0	-695	-695	US	3	67	336	185	70.0	6.2	3.56
	(NH4)2CO3/ NH4HCO3 pH 7	0.52/ 0.3	KMnO4	0.003	50.00	48.05	7.8	7.8	-33	556	386	US	3	67	328	83.4	86.1	9.9	1.60
112	H2SO4	0.5	KMnO4	0.003	59.99	N/A	0.5	0.5	-	620	633	RECIRC	0.5	39	288	71.2	87.7	N/A	1.37
	H2SO4	0.5	KMnO4	0.003	22.36	N/A	0.5	0.4	-	838	506	RECIRC	0.5	37	303	38.2	93.4	N/A	0.73
113	H2SO4	0.5	KMnO4	0.003	60.00	N/A	0.5	0.4	-	610	559	RECIRC	1	38	303	73.3	87.3	N/A	1.41
	H2SO4	0.5	KMnO4	0.003	20.4	N/A	0.5	0.5	-	1033	498	RECIRC	1	40	303	40.0	93.1	N/A	0.77
114	H2SO4	0.5	KMnO4	0.003	60.00	N/A	0.4	0.4	-	590	590	RECIRC	1.5	39	303	75.5	87.0	N/A	1.45
	H2SO4	0.5	KMnO4	0.003	29.54	N/A	0.5	0.3	-	781	625	RECIRC	1.5	39	303	36.1	93.8	N/A	0.69
115	H2SO4	0.5	KMnO4	0.003	60.00	N/A	0.3	0.3	-	563	612	RECIRC	3	39	303	73.2	87.3	N/A	1.41
	H2SO4	0.5	KMnO4	0.003	29.66	N/A	0.3	0.3	-	789	695	RECIRC	3	39	303	36.8	93.6	N/A	0.71
116	H2SO4	0.5	KMnO4	0.003	60.02	N/A	0.7	0.7	-	714	758	RECIRC	1.7	40	85	75.2	87.0	N/A	1.45
	H2SO4	0.5	KMnO4	0.003	24.05	N/A	0.6	0.6	-	899	1050	RECIRC	1.7	40	85	45.4	92.1	N/A	0.87
117	H2SO4	0.5	KMnO4	0.003	60.01	N/A	0.6	0.7	-	890	875	RECIRC	3.6	40	85	81.8	85.9	N/A	1.57
	H2SO4	0.5	KMnO4	0.003	22.20	N/A	0.7	0.6	-	1163	906	RECIRC	3.6	40	85	48.0	91.7	N/A	0.92
118	H2SO4	0.5	KMnO4	0.003	60.00	N/A	0.5	0.5	-	642	718	RECIRC	5.4	40	85	80.1	86.2	N/A	1.54
	H2SO4	0.5	KMnO4	0.003	22.20	N/A	0.4	0.4	-	806	823	RECIRC	5.4	40	85	45.2	92.2	N/A	0.87
119	H2SO4	0.5	KMnO4	0.003	60.00	N/A	0.5	0.5	-	738	914	RECIRC	10.7	40	85	82.2	85.8	N/A	1.58
	H2SO4	0.5	KMnO4	0.003	22.26	N/A	0.4	0.4	-	843	790	RECIRC	10.7	40	85	41.5	92.8	N/A	0.80

Note: US - Ultrasonic Mixing + Magnetic Stirring
MECH - Mechanical Mixing
RECIRC - Ultrasonic Mixing in a Recirculatiing loop
ROT- Rotational Mixing
* - Concentration in g/L

Air* - 5 LPM Air@ STP / L of solution
efm vs Ag/AgCl (4M KCl) (reduction potential)
Eh = emf + 200mV
Solid:Liquid Ratio = 1:10 except serial number 92 at 1:5

TCLP Extraction Fluid #1 in Serial #48 and 49 refers to EPA designation for acetic acid buffer pH 4.93
PCRE - Percent Contamination Removal Efficiency
TSQI - Treated Soil Quality Index
A target guideline for treated soil of 52 ug/g (35 pCi/g) of soil was assigned to uranium concentration

Table B.13: Fernald Incinerator Area Soil Leaching - Other Metals Removal Results

	Analysis of Treated Soil by ICP in ug/g						Analysis of Treated Soil by ICP in ug/g				
Serial #	[Al]	[Ca]	[Fe]	[Mn]	[Pb]	Serial #	[Al]	[Ca]	[Fe]	[Mn]	[Pb]
34	6560	1060	13400	482	28.3	54	9030	2760	12100	142	20.5
35	6740	1250	13100	402	30.2	55	8810	886	10500	63	22.9
36	5310	798	11400	407	26.1	60	10200	974	16600	478	24.9
37	5660	1600	12600	518	30.5	61	10300	1620	17500	6315	27.3
38	5110	699	9890	293	23.2	62	10800	353	19500	609	28.1
39	5390	2510	11300	415	27.3	63	10700	529	20100	619	29.7
40	479	227	3350	331	40.5	64	10200	6530	19600	498	31.6
41	4520	433	664	227	22.7	65	10200	2740	18100	509	26.5
42	5440	1840	116	664	24.2	66	10000	2480	19000	591	31.6
43	4300	544	8820	281	27.7	67	8875	3405	17800	483	27.6
44	11900	699	16000	264	27.9	68	9400	8050	18700	597	29.5
45	12900	836	16400	215	27.3	69	9400	5900	18000	502	27.5
50	11600	3860	20000	547	29.3	70	9700	387	19500	635	31.3
51	11100	3840	19200	500	27.3	71	9390	2200	18000	557	29.9

Note:
1. For test conditions see Table B.12
2. For two stage experiments only the second stage treated soil was analyzed for metals.

Table B.14: Chalk River Chemical Pit Soil Leaching - Experimental Conditions, and Sr-90 and Gross Gamma Removal Results

TEST CONDITIONS / MEASURED QUANTITIES															CONC. OF SPECIES IN TREATED SOIL Activity (pCi/g)		CALCULATED RESULTS					
																	PCRE		Soil		TSQI	
Serial #	Leachant	Conc. mol/L	Redox Agent	Conc. g/g of soil	Feed wt. g	Residue wt. g	Initial pH	Final pH	Initial emf mV	Final emf mV	Mixing Method	Mean Temp. ° C	Time min.	Power Input W	Sr-90	Gross Gamma	Sr-90	Gross Gamma	Dissolution %	Sr-90	Gross Gamma	Total Activity
36	HCl	0.1	-	-	40.11	37.48	1.2	1.2	580	523	US	49	3	333	91.80	21.10	92.67	71.25	6.55	2.62	0.60	3.23
	HCl	0.1	-	-	18.71	20.42	1.2	1.1	556	534	US	46	3	333	56.70	29.38	96.12	65.72	6.55	1.62	0.84	2.46
37	HCl	0.5	-	-	40.04	37.48	0.5	0.4	551	550	US	50	3	333	94.50	23.24	93.53	72.83	6.39	2.70	0.66	3.36
	HCl	0.5	-	-	17.95	19.57	0.5	0.4	503	493	US	49	3	333	51.30	17.86	95.91	75.69	6.39	1.47	0.51	1.98
38	Water	-	Na2S2O4	0.002	20.02	-	7.8	6.9	23	- 500	US	51	3	352	-	-	-	-	-	-	-	-
	Conc. HCl to pH 1.2	-	-	-	-	19.16	7.1	1.3	- 44	555	US	56	3	356	45.90	21.92	96.79	73.81	4.30	1.31	0.63	1.94
39	Water	-	Na2S2O4	0.0015	20.02	-	7.5	6.7	98	- 461	US	52	3	346	-	-	-	-	-	-	-	-
	Conc. HCl to pH 1.2	-	-	-	-	19.17	7.1	0.6	- 37	530	US	56	3	358	45.90	6.49	96.78	92.23	4.25	1.31	0.19	1.50
40	Water	-	Na2S2O4	0.0035	20.03	-	7.7	7.0	8	-686	US	67	3	364	-	-	-	-	-	-	-	-
	Conc. HCl to pH 1.2	-	-	-	-	19.17	6.5	1.3	- 22	531	US	62	3	381	62.10	6.69	95.65	92.00	4.29	1.77	0.19	1.97
41	Water	-	Na2S2O4	0.0013	40.01	37.57	8.0	7.1	115	- 478	US	50	3	332	-	-	-	-	-	-	-	-
	Conc. HCl to pH 1.2	-	-	-	-	17.02	7.4	1.3	33	554	US	51	3	345	48.60	7.06	98.49	96.25	6.11	1.39	0.20	1.59
	Water	-	Na2S2O4	0.0178	20.29	-	2.9	3.4	- 372	225	US	52	3	385	-	-	-	-	-	-	-	-
	Conc. HCl to pH 1.2	-	-	-	-	19.65	3.8	1.2	- 6	225	US	57	3	364	32.40	6.47	97.70	92.17	9.05	0.93	0.18	1.11
42	HCl	0.5	Na2S2O4	0.066	40.01	37.24	0.5	0.5	542	39	US	45	3	333	43.20	17.91	97.06	79.18	6.92	-	-	-
	HCl	0.5	Na2S2O4	0.043	18.52	20.14	0.4	0.3	275	145	US	47	3	333	37.80	14.78	96.99	79.93	6.92	1.08	0.42	1.50
60	TCLP Extraction Fluid #1	-	-	-	100.00	81.24	4.9	4.9	-	-	ROT	25	1140	-	286.20	182.52	80.75	0.00	18.76	8.18	5.21	13.39
61	TCLP Extraction Fluid #1	-	-	-	100.02	95.95	4.9	4.9	-	-	ROT	25	1140	-	429.30	243.54	69.87	0.00	4.07	12.27	6.96	19.22
85	HCl	0.5	-	-	30.01	-	0.6	0.7	453	483	US/RECIRC	39	0.5	284	205.96	49.46	82.81	95.87	-	5.88	1.41	7.30
86	HCl	0.5	-	-	30.01	-	0.6	0.5	503	485	US/RECIRC	40	1	282	192.41	47.34	83.94	96.05	-	5.50	1.35	6.85
87	HCl	0.5	-	-	30.01	-	0.5	0.6	480	422	US/RECIRC	40	1.5	281	135.50	44.15	88.69	96.32	-	3.87	1.26	5.13
88	HCl	0.5	-	-	30.03	-	0.6	0.5	487	441	US/RECIRC	40	3	281	130.08	43.12	89.15	96.40	-	3.72	1.23	4.95
89	HCl	0.5	-	-	30.00	29.13	0.6	0.6	515	521	MECH	40	1.7	85	102.98	44.17	91.66	57.86	-	2.94	1.26	4.20
90	HCl	0.5	-	-	30.00	29.22	0.5	0.7	535	524	MECH	40	3.3	85	102.98	45.26	91.63	56.70	-	2.94	1.29	4.24
91	HCl	0.5	-	-	30.01	29.07	0.7	0.7	531	525	MECH	40	5.0	85	84.01	42.28	93.21	59.77	-	2.40	1.21	3.61
92	HCl	0.5	-	-	30.00	27.28	0.7	0.7	534	534	MECH	40	10.0	85	67.75	42.55	94.86	61.99	-	1.94	1.22	3.15
93	HCl	0.5	Na2S2O4	0.05	60.01	-	0.3	0.5	180	144	US/RECIRC	39	0.5	304	124.66	53.66	89.60	47.29	-	3.56	1.53	5.09
	HCl	0.5	Na2S2O4	0.05	25.12	-	0.4	0.4	258	156	US/RECIRC	39	0.5	304	29.81	48.24	97.51	52.61	-	0.85	1.38	2.23
94	HCl	0.5	Na2S2O4	0.05	60.02	-	0.2	0.5	228	144	US/RECIRC	39	1.0	303	130.08	50.95	89.15	49.95	-	3.72	1.46	5.17
	HCl	0.5	Na2S2O4	0.05	25.25	-	0.2	0.4	235	163	US/RECIRC	39	1.0	304	56.91	53.66	95.25	47.29	-	1.63	1.53	3.16
95	HCl	0.5	Na2S2O4	0.05	60.00	-	0.5	0.5	263	190	US/RECIRC	39	1.5	304	70.46	49.86	94.12	51.01	-	2.01	1.42	3.44
	HCl	0.5	Na2S2O4	0.05	26.48	-	0.5	0.5	293	203	US/RECIRC	40	1.5	304	67.75	55.68	94.35	45.30	-	1.94	1.59	3.53
96	HCl	0.5	Na2S2O4	0.05	60.01	-	0.5	0.6	378	200	US/RECIRC	40	3.0	303	105.69	52.57	91.18	48.35	-	3.02	1.50	4.52
	HCl	0.5	Na2S2O4	0.05	25.49	-	0.5	0.6	329	213	US/RECIRC	40	3.0	303	35.23	48.45	97.06	52.40	-	1.01	1.38	2.39
97	HCl	0.5	Na2S2O4	0.05	60.02	60.61	0.6	0.7	180	256	MECH	39	1.8	85	89.43	43.09	92.46	57.25	-	2.56	1.23	3.79
	HCl	0.5	Na2S2O4	0.05	29.61	26.94	0.5	0.6	329	213	MECH	40	1.8	85	56.91	44.99	95.68	59.79	-	1.63	1.29	2.91
98	HCl	0.5	Na2S2O4	0.05	60.03	57.61	0.7	0.7	137	235	MECH	40	3.6	85	94.85	42.01	92.40	60.40	-	2.71	1.20	3.91
	HCl	0.5	Na2S2O4	0.05	24.90	25.05	0.9	0.9	237	253	MECH	40	3.6	85	35.23	34.96	97.04	65.44	-	1.01	1.00	2.01
99	HCl	0.5	Na2S2O4	0.05	60.01	60.84	0.9	0.9	151	226	MECH	40	5.4	85	43.36	35.50	96.33	64.64	-	1.24	1.01	2.25
	HCl	0.5	Na2S2O4	0.05	30.22	27.49	0.9	0.9	187	274	MECH	40	5.4	85	21.68	25.20	98.35	77.48	-	0.62	0.72	1.34
100	HCl	0.5	Na2S2O4	0.05	60.01	57.59	0.9	0.9	-125	428	MECH	39	10.7	85	40.65	36.85	96.74	65.26	-	1.16	1.05	2.21
	HCl	0.5	Na2S2O4	0.05	24.90	25.29	0.9	0.8	720	468	MECH	40	10.7	85	35.23	30.79	97.01	69.27	-	1.01	0.88	1.89

Note:

* concentration in mol/L
† concentration in g/L
Gross gamma = cobalt-60 + cesium-137
PCRE - Percent Contamination Removal Efficiency

US - Ultrasonic Mixing
MECH - Mechanical Mixing
ROT - Rotational Mixing

emf vs Ag/AgCl (4 M KCl) (*reduction potential*)
Eh = emf + 200 mV
Solid:Liquid Ratio = 1:10

TSQI - Treated Soil Quality Index
TCLP Extraction Fluid #1 - Acetic Acid/Acetate Buffer pH 4.93
A target guideline for Treated Soil of 35 pCi/g is assigned individually to strontium-90 (beta) and gross gamma (sum of cobalt-60 & cesium-137)

Table B.15: Fernald Incinerator Area Soil - Leachate Assay

			Metal Concentration (mg/L)									FWQI U
Feed Serial #	Leachant	pH	[U]	[Al]	[Ca]	[Fe]	[Mg]	[Mn]	[Pb]	[SO4]	TDS	
93	H2SO4	1.1	38.8	-	-	-	-	-	-	-	-	647
94	H2SO4	1.5	42.1	-	697	268	-	-	-	19500	24100	702
95	H2SO4	0.9	40.7	-	787	467	176	-	-	27200	34000	678
96	H2SO4	0.6	57.8	238	748	441	-	261	< 0.8	-	64900	963

Note: FWQI - Feed Water Quality Index = ([U] / 0.06)
A target guideline for produced water of 0.060 mg/L was assigned to uranium concentration

Table B.16: Fernald Incinerator Area Soil - Leachate Treatment: Selected Metals Removal Results

	Metal Concentration in the Treated Leachate (mg/L)								
Feed Serial #	[U]	[Al]	[Ca]	[Fe]	[Mg]	[Mn]	[Pb]	[SO4]	TDS
95	31.70	-	474	323	-	-	-	4540	-
	4.96	-	781	0.3	-	-	-	2170	3600*
94	10.70	-	610	0.11	-	-	-	2070	3440
94	8.34	-	626	0.03	-	-	-	2120	3460
94	1.70	-	640	0.06	-	-	-	1700	2680
94	0.51	-	609	0.08	-	-	-	2020	3600
95	12.70	-		0.23	4770	-	-	26400	-
95	18.70	-	-	0.12	5000	-	-	26300	-
95	8.90	-	-	0.27	5050	-	-	25300	-
96	30.40	0.7	718	0.08	-	166	< 0.0	-	110000
	0.11	< 0.1	551	< 0.0	-	0.02	< 0.0	-	67300

Table B.17: Fernald Incinerator Area Soil - Leachate Treatment: Uranium Removal Results

Feed Serial #	Conc. g/L	Precipitant Agent	Oxidant/Precipitant Conc ug/g soln.	Oxidant/Precipitant Agent	Scavenging Conc ug/g soln	Scavenging Agent	Feed Soln Volume mL	Feed Soln Matrix	Initial pH	Final pH	Mixing Method	Mean Temp. ° C	Treatment Time min.	Power Input W	[U] mg/L	PCRE U %	PWQI (*)	PWQI (**)
95(a)	17.4	Ca(OH)2	-	-	-		750	H2SO4	0.9	4.3	RECIRC	26	1	371	31.70	22.11	528.3	109.3
95(b)	2.9	Ca(OH)2	1500	H2O2	100	Fe3+	500		4.2	9.8	RECIRC	25	1	374	0.11	99.72	1.8	0.4
93	18.0	Ca(OH)2	1500	H2O2	100	Fe3+	200	H2SO4	1.1	7.2	US	30	3	309	4.96	87.22	82.7	17.1
94	14.7	Ca(OH)2	1500	H2O2	100	Fe3+	750	H2SO4	1.5	8.4	RECIRC	26	3	370	10.70	74.58	178.3	36.9
94	15.2	Ca(OH)2	1500	H2O2	100	Fe3+	750	H2SO4	1.1	8.5	RECIRC	26	1	353	8.34	80.19	139.0	28.8
94	14.3	Ca(OH)2	1560	H2O2	-		750	H2SO4	1.4	9.5	RECIRC	24	3	346	0.56	98.67	9.3	1.9
93	30.0	CaCO3	1500	H2O2	100	Fe3+	200	H2SO4	1.1	6.0	US	27	3	319	1.70	95.62	28.3	5.9
94	30.0	CaCO3	1500	H2O2	100	Fe3+	750	H2SO4	1.5	6.4	RECIRC	25	3	344	0.51	98.79	8.5	1.8
95	29.4	Mg(OH)2	-	-	-		750	H2SO4	0.5	8.4	RECIRC	25	1	374	12.70	68.80	211.7	43.8
95	30.0	Mg(OH)2	-	-	-		750	H2SO4	0.6	8.5	RECIRC	26	3	346	18.70	54.05	311.7	64.5
95	23.8	Mg(OH)2	1500	H2O2	-		750	H2SO4	1.0	8.3	RECIRC	25	1	362	8.90	78.13	148.3	30.7
96(a)	31.3	Mg(OH)2	-		-		425	H2SO4	0.6	8.2	US	35	3	327	30.40	47.40	506.7	104.8
96(b)	64.7	NaOH (sat.)	1500	H2O2	50	Fe3+	300		8.2	9.7	US	31	3	327	0.11	99.81	1.8	0.4

Note: 1. (a) and (b) refer to *separate treatment of the filtrate from the first treatment stage*
2. Power input = line voltage x current
3. (*): (U concentration in the treated leachate in mg/L) / (U.S. drinking water limit, 0.06 mg/L)
4. (**): (U concentration in the treated leachate in mg/L) / (ICRP 1997 limit for maximum allowable concentration, 0.29 mg/L)

RECIRC - Ultrasonic Mixing in a Recirculating loop (Flow Rate = 3.0 L/min)
US - Ultrasonic Mixing + Magnetic Stirring
ROT - Rotational Mixing
MECH - Mechanical Mixing

Table B.18: Chalk River Chemical Pit Soil-Leachate Assay

Serial #	Feed Solution Matrix	Activity (pCi/L)			Metal Conc (mg/L)			TDS (mg/L)		FWQI Gross g	Total Activity
		Sr-90	Co-60	Cs-137	Ca	Fe	U		Sr-90		
62	HCl	129600	1080	263	-	-	-	-	13714	28	13742
64	HCl	123660	3159	540	95	193	0.27	2560	13086	57	13143
65	HCl	121500	3483	540	112	208	2.74	4540	12857	57	12914

Table B.19: Chalk River Chemical Pit Soil-Leachate Treatment Results

TEST CONDITIONS / MEASURED QUANTITIES										TREATED LEACHATE						CALCULATED RESULTS						
										Activity (pCi/L)		Metal Concentration (mg/L)				PCRE		PWQI(*)		PWQI (**)		
Feed Solution Serial #	Precipitant	Feed Soln. Vol mL	Feed Solution Matrix	Initial pH	Final pH	Mixing Method	Mean Pptn. Temp. ° C	Pptn. Time min.	Power Input W	Sr-90	Gross Gamma	Ca	Fe	U	TDS mg/L	Sr-90	Gross Gamma	Sr-90	U	Sr-90	Gross Gamma	U
62	0.50 g of Ca(OH)2	200	HCl	2.1	-	US	27	3	303	-	-	-	-	-	-	-	-	-	-	-	-	-
-	0.80 g of Na2CO3	-	-	-	11.1	US	37	3	301	634.5	975.0	-	-	-	-	99.51	27.40	66.8	-	2.4	0.4	-
64	2.50 g of Ca(OH)2	200	HCl	0.8	10.1	US	26	0.5	320	-	-	-	-	-	-	-	-	-	-	-	-	-
-	3.63 g of Na2CO3	-	-	9.6	9.9	US	30	0.5	320	324.0	1979.1	5.37	0.278	0.740	20800	99.74	46.50	34.1	12.3	1.2	0.7	2.6
64	2.45 g of Ca(OH)2	200	HCl	0.8	10.1	US	30	1	320	-	-	-	-	-	-	-	-	-	-	-	-	-
-	3.63 g of Na2CO3	-	-	9.8	10.1	US	37	1	320	278.1	1458.0	4.47	0.203	0.078	20700	99.78	60.58	29.3	1.3	1.0	0.5	0.3
64	2.69 g of Ca(OH)2	200	HCl	0.8	10.0	US	29	3	320	-	-	-	-	-	-	-	-	-	-	-	-	-
-	3.63 g of Na2CO3	-	-	10.2	9.8	US	41	3	320	313.2	3493.8	2.67	0.042	0.100	21000	99.75	5.55	33.0	1.7	1.2	1.3	0.3
64	2.78 g of Ca(OH)2	200	HCl	0.9	9.9	US	26	0.5	319	-	-	-	-	-	-	-	-	-	-	-	-	-
-	3.70 g of Na2CO3	-	-	-	10.1	US	30	0.5	322	-	-	-	-	-	-	-	-	-	-	-	-	-
-	0.41 g TSM 140 H zeolite	-	-	-	9.9	US	31	0.5	323	378.0	1933.2	5.93	0.042	0.090	21300	99.69	47.74	39.8	1.5	1.4	0.7	0.3
64	2.80 g of Ca(OH)2	200	HCl	0.9	11.1	US	26	0.5	323	-	-	-	-	-	-	-	-	-	-	-	-	-
-	3.70 g of Na2CO3	-	-	-	11.1	US	30	0.5	328	-	-	-	-	-	-	-	-	-	-	-	-	-
-	0.40 g TSM 140 H zeolite	-	-	-	10.9	US	33	1	327	108.0	1260.9	7.36	0.124	0.064	21500	99.91	65.91	11.4	1.1	0.4	0.5	0.2
64	2.70 g of Ca(OH)2	200	HCl	0.9	10.3	US	27	0.5	332	-	-	-	-	-	-	-	-	-	-	-	-	-
-	3.70 g of Na2CO3	-	-	-	10.4	US	31	0.5	328	-	-	-	-	-	-	-	-	-	-	-	-	-
-	0.41 g TSM 140 H zeolite	-	-	-	10.2	US	37	3	333	337.5	1377.0	5.08	0.051	0.170	21200	99.73	62.77	35.5	2.8	1.3	0.5	0.6
65	5.31 g Ca(OH)2 +	400	HCl	0.7	10.5	US	26	1	320	-	-	-	-	-	-	-	-	-	-	-	-	-
-	7.97 g Na2CO3 +	-	-	-	10.4	US	31	1	320	-	-	-	-	-	-	-	-	-	-	-	-	-
-	0.40 g TSM 140 H zeolite +	-	-	10.5	10.4	US	32	1	320	108.0	1080.0	3.06	0.073	0.183	26800	99.91	73.15	11.4	3.1	0.4	0.4	0.6
-	0.28 g TSM 140 H zeolite	275	-	-	10.4	US	27	3	320	189.0	540.0	7.20	0.062	0.202	27100	99.84	86.58	19.9	3.4	0.7	0.2	0.7
65	5.31 g Ca(OH)2 +	400	HCl	0.7	10.1	US	27	1	320	-	-	-	-	-	-	-	-	-	-	-	-	-
-	7.97 g Na2CO3 +	-	-	-	10.3	US	31	1	320	-	-	-	-	-	-	-	-	-	-	-	-	-
-	0.40 g TSM 140 H zeolite +	-	-	-	10.2	US	32	1	320	108.0	1080.0	2.96	0.053	0.180	25300	99.91	73.15	11.4	3.0	0.4	0.4	0.6
-	CO2 to pH 7 +	275	-	10.4	6.9	US	27	1	320	-	-	-	-	-	-	-	-	-	-	-	-	-
-	0.091g CuSO4 / 0.11g K4Fe(CN)	-	-	-	7.4	US	30	2	320	54.0	783.0	2.62	5.450	0.221	24600	99.96	80.54	5.7	3.7	0.2	0.3	0.8

PWQI Calculation:

(*) PWQI = *(contaminant concentration in treated leachate) / (corresponding contaminant limit in U.S. drinking water)*
U.S. drinking water limit: [Sr-90] = 9.5 pCi/L and [U] = 0.06 mg/L

(**) PWQI = (contaminant concentration in treated leachate) / (corresponding contaminant limit based on ICRP 1977 Maximum Allowable Concentration in water)
ICRP 1977 Maximum Allowable Concentration in water: [Sr-90] = 270 pCi/L; [U] = 0.29 mg/L, and [Gross Gamma] = 2700 pCi/L

Table B.20: Preliminary Process Parameters for the Integrated Soil Decontamination and Soil-Leachate Treatment

Parameter	Fernald Incinerator Area Soil	Chalk River Chemical Pit Soil
Process System Configuration	Closed loop	Closed loop
Soil Treatment (to remove primary contaminants)		
Primary Contaminant:	Uranium	Sr-90, Co-60, Cs-137, and U (trace levels)
Soil Preparation:		
Prescreening	To remove gravel	To remove gravel
Grinding	None	None
Soil Leaching:		
Mixing / Energy	Ultrasonically-aided	Ultrasonically-aided / ~135 kJ/L per stage
Soil/Liquid Ratio	1:10	1:10 / stage
Leaching Time	3 min	3 min / stage
Temperature	50 °C	Ambient to 50 °C (preferably 50 °C)
Leachant	0.1-0.5 mol/L H_2SO_4 TSQI 2 to 0.7	0.1 mol/L HCl
Additives:		
Redox Agents	$KMnO_4$/Air	$Na_2S_2O_4$ (small amounts required)
emf	>600 mV	<300 mV
Solid-Liquid Separation	May require flocculant	Not required
Wash Water	Yes	Yes
No. of Leaching Stages	1 (TSQI 1.5 - 2) 2 (TSQI 0.7 - 1)	1 to obtain TSQI of 1.5 2 to obtain TSQI of ≤ 1
Soil-Leachate Treatment (to remove primary and some secondary contaminants)		
Mixing / Energy	Ultrasonically-aided 35-160 kJ/L	Ultrasonically-aided / 35-160 kJ/L
Time for precipitation/ Sorption	1-3 min / stage	1-3 min
Temperature	Ambient	Ambient
Precipitating Agents	Lime, NaOH or Magnesia and H_2O_2 and Fe^{3+} (pH 8.5 - 10.5)	Lime, Soda
Sorbent	--	Natural Zeolite Powder
Solid-Liquid Separation	Yes	Yes
No. of Leaching Stages	1 (PWQI 10) 2 (PWQI 1)	

Table B.20 (continued)

Parameter	Fernald Incinerator Area Soil	Chalk River Chemical Pit Soil
<u>**Polishing System**</u> (to remove/control sulphate, chloride and Total Dissolved Solids)		
Chemical Addition	May require biodegradation of SO_4	None
Method (Waste Volume Reduction)		Nanofiltration

Table B.21: Summary of Column Test Parameters and Leaching Efficiencies

Soil Source: ES-31 Composite		Column	
Column Inside Diameter: 4.7 cm			
Column Length: 15.0 cm	B	C	D
Test Duration (h)	34.5	47.5	50.0
Leaching Agent	$Na_2S_2O_4$ - 0.1 mol/L HCl	0.1 mol/L HCl	0.1 mol/L HCl
Temperature (°C)	5	5	25
Flow Rate (mL/h)	41.7	22.1	17.4
Mass of Soil (g)	419.29	379.58	400.09
Porosity	0.39	0.45	0.42
Dispersivity (cm)	0.06	0.15	0.13
Pore Volume (mL)	106.0	114.5	104.1
Total Pore Volumes Added	11.85	9.4	8.05
Initial Inventory: ^{90}Sr (Bq)	3 359	3 040	3 205
Initial Inventory: ^{60}Co (Bq)	226	205	216
Initial Conc.: ^{90}Sr (Bq/g)	8.0	8.0	8.0
Initial Conc.: ^{60}Co (Bq/g)	0.54	0.54	0.54
^{90}Sr Removal-Column Elution Data (%)	117	83.2	91.3
^{90}Sr Removal-Soil Data (%)	88.9	90.5	90.3
^{60}Co Removal-Column Elution Data (%)	63	40	68
^{60}Co Removal-Soil Data (%)	62	67	92
@ 3 pore volumes :			
^{90}Sr Removal-Column Elution Data (%)	100	78	81
^{60}Co Removal-Column Elution Data (%)	149	150	N/A

Table B.22: **Percentage of ^{90}Sr and ^{60}Co Removed in the Field Test Cell and the Leachable Fractions of These Isotopes in the Post-Experiment Soils**

	^{90}Sr (Bq/g)	% of Initial ^{90}Sr	% of Final ^{90}Sr	^{60}Co (Bq/g)	% of Initial ^{60}Co	% of Final ^{60}Co
Average Concentration in the Test Cell	9.56			0.27		
Average of Individual Post-Test Core Samples:						
Bin-10	1.98±0.61	21±6		0.36±0.100	132±37	
Bin-11	1.07±0.45	11±5		0.29±0.08	104±28	
Bin-12	0.16±0.35	1.6±3.7		0.14±0.06	49±20	
Average of Composite Post-Test Core Samples:						
Bin-10	1.58±0.14	17±8		0.35±0.080	127±29	
Bin-11	0.81±0.13	8.5±1.4		0.22±0.07	80±24	
Bin-12	0.33±0.11	3.4±1.2		0.16±0.06	60±22	
Post-Citrate/Dithionite Leach Composite Concentrations:						
Bin-10	0.74±0.13		47±8	0.11±0.16		32±47
Bin-11	0.23±0.12		28±15	0.16±0.15		74±70
Bin-12	0.14±0.12		43±36	0.23±0.15		141±94

Note: 1) Number of pore volumes of sodium dithionite solution (average concentration: 930 mg/L) injected: 1.34
2) Number of pore volumes of hydrochloric acid solution (average 0.1 mol/L HCl) injected: 3.4
3) Number of pore volumes of water injected after hydrochloric acid: 1.97
4) Average flowrate of solution injected: 570 mL/min [450 - 634 mL/min]
5) One pore volume: approximately 4 100 litres
6) Overall soil to liquid ratio: approximately 1:2

Table B.23: Summary of Pilot-Scale Ex-Situ Chalk River Soil Leaching Results

Test Number	Soil Drum	Wt. of Soil (kg)	Wt. of Water (kg)	L/S Ratio	HCl Conc (Mol/L)	Wt. of Treated Soil (kg)	% Soil Loss	Mixing Method		Leaching Time (min)	Mean Temp (C)	Average pH	Average Eh (mV)	US Power Input (W)	Sr-90 Concentration (Bq/g) Feed	Sr-90 Concentration (Bq/g) Treated	Sr-90 Concentration PCRE (%)	Gross Gamma (Bq/g) Feed	Gross Gamma (Bq/g) Treated	Gross Gamma PCRE (%)	TSQI (Beta + Gamma
Feed 1	B4														18.2			0.58			
Feed 2	B4														19.7			0.59			
C1	B4	30.3	370	12.2	0.11	26.4	12.7	UST & Mech		60	30	1.3	736	472	18.2	1.40	92.3	0.58	0.27	53.4	1.3
C2	B4	30.1	300	10.0	0.13	27.6	8.2	UST & Mech		60	38	1.3	726	472	18.2	0.65	96.4	0.58	0.21	63.8	0.7
C3	B4	30.1	300	10.0	0.13	28.4	5.6	Mech		60	43	1.3	721	0	18.2	0.92	94.9	0.58	0.28	51.7	0.9
									Total Contact Time (min)	US Contact Time (min)											
C4a	B4	30.5	300	9.8	0.13	28.6	6.2	USF & Mech	0.78	0.06	23	1.1	743	713	18.2	2.44	86.6	0.58	0.31	46.6	2.1
C4b	B4	28.6	300	10.5	0.10	25.9	9.6	USF & Mech	0.15	0.03	24	1.1	716	713	3.5	1.89	46.0	-	-	-	-
C5	B3	30.9	300	9.7	0.05	27.8	9.8	USF & Mech	0.35	0.07	26	1.5	742	713	20.7	3.15	84.8	0.55	0.365	33.4	2.7
C6	B3	29.9	300	10.0	0.05	27.3	8.7	USF & Mech	0.35	0.07	10	1.7	742	713	19.9	4.37	78.0	0.52	0.398	23.5	3.7

Note: "a" denotes stage-1 leaching and "b" denotes stage-2 leaching.
UST: Mixing in Ultrasonic Tank
USF: Mixing in Ultrasonic Liquid Processor
Mech: Mechanically-Agitated Head Tank Combined with Pump and Flow Mixing
PCRE: Percent Contaminant Removal Efficiency

Table B.24: Pilot-Scale Chalk River Soil Leaching with Water and 0.05 mol/L HCl with or without Ultrasonic Mixing - Test Conditions and Results

Task No.:	3.3.5 (C5)

Soil:	Ground Chemical Pit Soil (B4)
Wt. of Soil:	30.9 kg
Wt. of Water:	300 kg
L/S Ratio:	9.71
HCl Conc.:	0.05 mol/L
HCl Added:	1.7 kg

Run Time:	30 min
Process Flow Rate:	10.00 L/min
Contact Time:	0.07 min

US Liquid Processor Setting:(30 kHz)	
Power:	100 %

Soil Leaching Data:

Sampling Time (min)	Temp (C)	ORP (mV)	Eh (mV)	pH	Ultrasonic Mixing Current (A)	Ultrasonic Mixing Voltage (V)	Ultrasonic Mixing Power (W)	Sample Code	Sr-90 (Bq/g)	Co-60 (Bq/g)	Ru-106 (Bq/g)	Cs-137 (Bq/g)	Am-241 (Bq/g)	Gross Gamma (Bq/g)
								M818	28.60	0.35	<0.15	<0.02	<0.03	0.55
Reference			200					M819/20	20	0.44	<0.11	<0.02	<0.02	0.59
0 (Water)	26	176	376	6.8	0	0	0	M821	21.60	0.41	<0.13	0.04	0.03	0.61
7	26	535	735	1.5	0	0	0	M822	2.08	0.16	<0.06	0.02	<0.01	0.25
12	26	543	743	1.8	3.1	230	713	M823	2.94	0.20	<0.06	0.02	<0.01	0.29
20	27	545	745	1.6	3.1	230	713	M824	1.98	0.14	<0.07	0.02	<0.01	0.25
25	26	544	744	1.6	0	0	0	M825	1.81	0.18	<0.07	<0.01	<0.01	0.27
30	27	543	743	1.5	0	0	0	M826	1.90	0.17	<0.07	0.03	<0.01	0.28
Average:	26	542	742	1.6										

Filter Pressing Data:

Feed Volume:	300 L	Loading Period:	10 min		
Filter-Aid Added:	1.2 kg 800S	Filtering Period:	40 min		
Op. Pressure:	40 psig	Washing Period:	8 min		
Op. Temp:	25 C	Wash Water Vol.:	100 L		
Air Dry:	yes	Total Filtration Time:	58 min		
Wet Weight:	0.08672 kg				
Dry Weight:	0.07643 kg				
Wt. of Water:	0.01029 kg				
Moisture content:	11.87 %				
Soilds Content:	88.13 %				
Treated Soil Wt.:	33.00 kg	Corr. Wt:	27.88 kg	% Loss:	9.76

		Sr-90 (Bq/g)	Co-60 (Bq/g)	Ru-106 (Bq/g)	Cs-137 (Bq/g)	Am-241 (Bq/g)	Gross Gamma (Bq/g)
Wet Cake Sample:	M828	3.15	0.22	<0.09	0.04	<0.01	0.37
Filtrate Sample:							

Table B.25: Pilot-Scale Chalk River Soil Leaching with Water and 0.13 mol/L HCl with or without Ultrasonic Mixing - Test Conditions and Results

Task No.:	3.3.4a (C4a)

Soil:	Ground Chalk River Soil (B4)
Wt. of Soil:	30.5 kg
Wt. of Water:	300 kg
L/S Ratio:	9.84
HCl Conc.:	0.13 mol/L
HCl Added:	4.2 kg

Run Time:	28 min
Process Flow Rate:	10.71 L/min
Contact Time:	0.06 min

US Liquid Processor Setting:(30 kHz)	
Power:	100 %

Soil Leaching Data:

Sampling Time (min)	Temp. (C)	ORP (mV)	Eh (mV)	pH	Ultrasonic Mixing Current (A)	Ultrasonic Mixing Voltage (V)	Ultrasonic Mixing Power (W)	Sample Code	Sr-90 (Bq/g)	Co-60 (Bq/g)	Ru-106 (Bq/g)	Cs-137 (Bq/g)	Am-241 (Bq/g)	Gross Gamma (Bq/g)
							(Top Feed)	M776*	18.20	0.44	<0.11	<0.02	<0.02	0.58
Reference			200				(Feed)	M777*	19.70	0.41	<0.11	0.05	<0.02	0.59
0 (Water)	23	366	566	6.8	3.1	230	713	M778*	10.80	0.31	<0.08	0.03	<0.02	0.42
7	24	532	732	1.0	3.1	230	713	M779						
12	24	546	746	1.1	3.1	230	713	M780	2.06	0.39	<0.09	0.05	<0.02	0.55
17	24	548	748	1.3	3.1	230	713	M781*	4.20	0.39	<0.09	0.06	<0.02	0.55
20	24	547	747	1.1	3.1	230	713	M782*	4.64					
Average:	23	508	743	1.1	3.1	230	713							

Filter Pressing Data:

Feed Volume:	300 L	Loading Period:	10 min		
Filter-Aid Added:	1 kg 800S	Filtering Period:	30 min		
Op. Pressure:	0-40 psig	Washing Period:	10 min		
Op. Temp:	25 C	Wash Water Vol.:	200 L		
Air Dry:	yes	Total Filtration Time:	50 min		
Wet Weight:	0.338 kg				
Dry Weight:	0.268 kg				
Wt. of Water:	0.07 kg				
Moisture content:	20.71 %				
Soilds Content:	79.29 %				
Treated Soil Wt.:	33.80 kg	Corr. Wt:	28.60 kg	% Loss:	6.23

		Sr-90 (Bq/g)	Co-60 (Bq/g)	Ru-106 (Bq/g)	Cs-137 (Bq/g)	Am-241 (Bq/g)	Gross Gamma (Bq/g)
Wet Cake Sample:	M783*	2.44	0.20	<0.07	0.03	<0.01	0.31
Filtrate Sample:							

Table B.26: Summary of Pilot-Scale Chalk River Soil Leachate Treatment Results

Test Conditions

Test Number	Soil Leaching Test No.	Stage No.	Feed Volume (L)	Wt. of Lime (kg)	Wt. of Soda (kg)	Type of Adsobent	Dosage of Adsobent (mg/kg)	Mixing Method	Mixing Time (min)	Mean Temp (C)	Average pH	Average Eh (mV)	Ultrasonic Power Input (W)	Wt. of Dry Secondary Waste (kg)
CL3	C3	1	800	1.70	3.10			Flow	300	27	11.5	183	0	(*) 2.40
CL4a	C4a	1	500	1.70	6.40			USF/Flow	86	25	10.5	397	713	2.70
		2				Chabazite/MnO2	250/25		57				713	
CL4b	C4b	1	500	1.20	2.40			USF/Flow	87	26	11.0	574	713	
		2				Chabazite/MnO2	250/25		50				713	
CL5	C5	1	400	0.68	2.00			USF/Flow	70	28	11.3	259	713	1.70
						Chabazite/MnO2	250/25		40				713	
CL6	C6	1	300	0.57 (plus 1.2 kg NaOH)	1.70			USF/Flow	80	15	11.6	411	713	1.60

Test Results

Test Number	Soil Leaching Test No.	Stage No.	Sr-90 (Bq/L) Feed	Sr-90 (Bq/L) Treated	Sr-90 PCRE (%)	Calcium (mg/L) Feed	Calcium (mg/L) Treated	Calcium PCRE (%)	Iron (mg/L) Feed	Iron (mg/L) Treated	Iron PCRE (%)	Uranium (ug/L) Feed	Uranium (ug/L) Treated	Uranium PCRE (%)	TDS (mg/L) Feed	TDS (mg/L) Treated	TDS PCRE (%)
CL3	C3	1	583	9.82	98.3	851	7.51	99.1	14.9	0.104	99.3	22.5	3.3	85.3	3400	4540	-33.5
CL4a	C4a	1	950	21.5	97.7	1720	8.34	99.5	63.6	0.177	99.7	279	33	88.2	13300	4730	64.4
		2	21.5	16.1	25.1	8.34	4.35	47.8	0.177	0.02	88.7	33	39.3	-19.1	4730	4810	-1.7
CL4b	C4b	1	151	<12	>92.1	189	6.48	96.6	19.3	0.111	99.4	49.9	10.7	78.6	1020	4760	-366.7
		2	<12	<16	-33.3	6.48	13.9	-114.5	0.111	0.095	14.4	10.7	9.5	11.2	4760	4480	5.9
CL5	C5	1	1420	9.16	99.4	64	6.93	89.2	53.1	0.209	99.6	888	357	59.8	1360	4090	-200.7
		2	13.7	13.5	1.5	6.93	6.29	9.2	0.209	0.046	78.0	357	298	16.5	4090	4110	-0.5
CL6	C6	1	1380	17.2	98.8	52.2	16.8	67.8	59.8	0.591	99.0	207	153	16.1	1020	4470	-338.2

Note:
USF: Mixing in Ultrasonic Liquid Processor
Flow: Flow mixing in a Recirculation Loop via the Head Tank with no Mechanical Agitation
PCRE: Percent Contaminant Removal Efficiency
TDS: Total Dissolved solids
(*) The amount of secondary waste does not include the amount of about 1.2 kg filter-aid used during filtration. The amount of filter-aid used was excessive than what is needed in actual filtration operation. Typically about 5 to 10% (filter-aid to precipitate) filter-aid should be sufficient.

Table B.27: Pilot-scale Chalk River Soil Leachate Treatment By Lime-Soda Precipitation Followed by Sorption in an Ultrasonic Liquid Processor - Test Conditions and Results

Task No.:	3.4.5(CL5)

(A) Lime-Soda Treatment:

Volume:	400 L	Process Flow Rate:	5.679 L/min
Lime Added:	0.675 kg	Microfiltration Process:	No
Soda Added:	2 kg	Filtrate flow Rate:	N/A L/min

Time (min)	Process Temp. (C)	ORP (mV)	Eh (mV)	pH	Ultrasonic Mixing Current (A)	Ultrasonic Mixing Voltage (V)	Ultrasonic Mixing Power (W)	Sample Code	Sr-90 (Bq/L)	Co-60 (Bq/L)	Ru-106 (Bq/L)	Cs-137 (Bq/L)	Am-241 (Bq/L)	Gross Gamma (Bq/L)	Ca (mg/L)	Fe (mg/L)	U (ppb)	TDS (mg/L)
Reference		478	200	2.1				M829/30	1420	<0.03	<0.10	<0.01	<0.02	<0.15	64.00	53.10	888	1360
0	27	130	330	11.4	3.1	230	713											
15	27	69	269	11.4	3.1	230	713	M831/838	9.09	<0.01	<0.08	<0.01	<0.01	<0.11	5.56	0.19	396	4240
30	27	58	258	11.3	3.1	230	713											
45	28	56	256	11.3	3.1	230	713	M832/39	9.16	<0.02	<0.07	<0.01	<0.01	<0.10	5.65	0.26	357	4870
60	28	54	254	11.3	3.1	230	713											
70	28	60	260	11.0	3.1	230	713											
Average:	28	59	259	11.3	3.1	230	713											

(B) Additional Chemical Treatment

Wt of Chabazite:	0.1 kg	(250 ppm)
Wt of MnO2	0.01 kg	(25 ppm)

Filter Pressing Data:

Feed Volume:	400 L	Loading Period:	5 min
Filter-Aid Added:	1.2 kg 800S	Filtering Period:	55 min
Op. Pressure:	0-40 psig	Washing Period:	0 min
Op. Temp:	25 C	Wash Water Vol.:	0 L
Air Dry:	yes	Total Filtration Time:	60 min
Wet Weight:	0.0773 kg		
Dry Weight:	0.03 kg		
Wt. of Water:	0.0473 kg		
Moisture content:	61.19 %	Wet Cake Wt.:	7.4 kg
Soilds Content:	38.81 %	Solid Wt.:	2.87 kg

	Sample Code	Sr-90 (Bq/L)	Co-60 (Bq/L)	Ru-106 (Bq/L)	Cs-137 (Bq/L)	Am-241 (Bq/L)	Gross Gamma (Bq/L)	Ca (mg/L)	Fe (mg/L)	U (ppb)	TDS (mg/L)
	Filtrate Sample:										
	M833/40(Feed)	13.70	<0.01	<0.07	<0.01	<0.01	<0.10	6.93	0.209	357	4090
	M834/41(15 min)	14.60	<0.01	<0.07	<0.01	<0.01	<0.10	6.53	0.093	313	4150
	M835/42 (25 min)	12.60	<0.02	<0.07	<0.01	<0.01	<0.10	6.30	0.076	313	4160
	M836/43 (40 min)	13.5	<0.02	<0.08	<0.01	<0.01	<0.11	6.29	0.046	298	4110
Wet Cake Sample:	M837	88000	716	<300	<30	<50	<1096			148000	
Filtrate Sample:											

Table B.28: Pilot-Scale Chalk River Soil Leachate Treatment by Caustic-Lime-Soda Precipitation in an Ultrasonic Liquid Processor- Test Conditions and Results

Task No.:	CL6

(A) Lime-Soda Treatment:

Volume:	300 L	Process Flow Rate:	4.8 L/min
Lime Added:	0.57 kg		
NaOH Added:	1.2 kg	Microfiltration Process:	No
Soda Added:	1.7 kg	Filtrate flow Rate:	N/A L/min

Time (min)	Process Temp. (C)	ORP (mV)	Eh (mV)	pH	US I (A)	US V (V)	US Power (W)	Sample Code	Sr-90 (Bq/L)	Co-60 (Bq/L)	Ru-106 (Bq/L)	Cs-137 (Bq/L)	Am-241 (Bq/L)	Gross Gamma (Bq/L)	Ca (mg/L)	Fe (mg/L)	U (ppb)	TDS (mg/L)
Reference		485	200	2.0														
Feed	18	496	696	1.7				M1058	1380	<0.013	<0.079	<0.009	<0.010	<0.111	52.2	59.8	207	1020
Lime addition	18	354	554	4.4	3.1	230	713											
0	18	172	372	12.2	3.1	230	713	M1060	1440	<0.014	<0.076	<0.009	<0.011	<0.110	52.2	61.3	211	1190
5	18	210	410	12.1	3.1	230	713	M1062	51.1	<0.010	<0.076	<0.010	<0.009	<0.105	28.9	0.863	108	6310
10	17	161	361	11.7	3.1	230	713	M1064	29.3	<0.009	<0.073	<0.009	<0.009	<0.100	13.2	0.206	39.6	3210
20	18	210	410	11.6	3.1	230	713	M1066	20	<0.008	<0.070	<0.009	<0.010	<0.097	9.12	0.115	69	4070
							(before FP)	M1068	51.6	<0.010	<0.065	<0.007	<0.009	<0.091			91.6	
40	14	234	434	11.6	3.1	230	713	M1069	13.6	<0.009	<0.065	<0.008	<0.009	<0.091	5.31	0.102	82.2	4720
							(before FP)	M1071	61.1	<0.009	<0.070	<0.009	<0.010	<0.098			82.6	
55							(Feed)	M1072	1170	<0.010	<0.074	<0.009	<0.010	<0.103			105	
60	15	154	354	11.6	3.1	230	713	M1073	11.5	<0.010	<0.068	<0.008	<0.009	<0.095	3.92	0.102	106	5130
							(before FP)	M1075	45.5	<0.008	<0.071	<0.008	<0.009	<0.096			111	
80	15	247	447	11.8	3.1	230	713	M1076	10.1	<0.010	<0.073	<0.010	<0.009	<0.102	3.1	0.1	83.7	4790
Average:	15	211	411	11.6	3.1	230	713											

(B) Additional Chemical Treatment

Wt of Chabazite:	0 kg
Wt of MnO2	0 kg

Filter Pressing Data:

Feed Volume:	300 L	Loading Period:	5 min
Filter-Aid Added:	1 kg 700M	Filtering Period:	80 min
Op. Pressure:	0-40 psig	Washing Period:	0 min
Op. Temp:	25 C	Wash Water Vol.:	0 L
Air Dry:	yes	Total Filtration Time:	85 min
Wet Weight:	0.0878 kg		
Dry Weight:	0.0282 kg		
Wt. of Water:	0.0596 kg		
Moisture content:	67.88 %	Wet Cake Wt.:	8.059 kg
Solids Content:	32.12 %	Solid Wt.:	2.59 kg

	Sample Code	Sr-90 (Bq/L)	Co-60 (Bq/L)	Ru-106 (Bq/L)	Cs-137 (Bq/L)	Am-241 (Bq/L)	Gross Gamma (Bq/L)	Ca (mg/L)	Fe (mg/L)	U (ppb)	TDS (mg/L)
Wet Cake Sample:	M1081	213000	2060	<800	<100	254	<3214				
Filtrate Sample:	M1078	17.2	<0.010	<0.066	<0.008	<0.009	<0.093	16.8	0.591	153	4470

Table B.29: Summary of Test Conditions Used in Pilot-Scale Fernald Incinerator Area Soil Leaching

Test Number	Wt. of Soil (kg)	Wt. of Water (kg)	L/S Ratio	H2SO4 Conc (Mol/L)	Dosage of KMnO4 (kg/kg)	Wt. of Treated Soil (kg)	% Soil Loss	Mixing Method	Mean Temp (C)	Average pH	Average Eh (mV)	US Power Input (W)
F1	32.9	360	10.9	0.00	0.00			USF & Mech	24	6.9	335	0 or 713
F2	29.97	380	12.7	0.11	0.00	27.1	9.6	Mech	24	1.6	803	0
F3	30.15	300	10.0	0.14	0.00	27.6	8.3	USF & Mech	22	1.2	784	713
F4	30.79	360	11.7	0.25	0.03	27.9	9.3	USF & Mech	40	0.8	1161	713
F5 (**)	26.5	380	14.3	0.2 mol/L Na2CO3 & NaHCO3	0.00	24.7	6.7	USF & Mech	32	9.6	340	713
F6	30.41	390	12.8	0.23	0.03	27.5	9.7	Mech	40	0.8	1220	0
F7	30	400	13.3	0.23	0.03	27.1	9.7	USF & Mech	39	0.8	1166	713
F8	31.9	410	12.9	0.08	0.03	29.9	6.2	USF & Mech	42	1.2	1195	713

Note: USF: Mixing using Ultrasonic Liquid Processor
Mech: Mechanically-Agitated Head Tank Combined with Pump and Flow Mixing
(**): Test F5 using 0.2 mol/L sodium carbonate and 0.2 mol/L sodium bicarbonate as leachant
Slurry Flow Rate : 40 L/min

Table B.30: Summary of Pilot-Scale Fernald Soil Leaching Results

Test Number (*)	(A) U Concentration (mg/kg)			(B)				(C)				(D)		
	Dry Feed Soil	Soil After Contact With H2O	Reaction Time (sec)	U Conc. in Treated Soil (mg/kg)	PCRE (%)	TSQI	Reaction Time (Recirc) (min)	U Conc. in Treated Soil (mg/kg)	PCRE (%)	TSQI	Reaction Time (Recirc) (min)	U Conc. in Treated Soil (mg/kg)	PCRE (%)	TSQI
F1	498	546	N/A	-	-	-	7	532	2.6	10.20	30	503	7.9	9.70
F2	581	561	N/A	-	-	-	7	228	59.4	4.40	30	221	60.6	4.30
F3	606	728	N/A	-	-	-	7	388	46.7	7.50	30	190	73.9	3.60
F4	529	658	~1	129	80.4	2.50	8	112	83.0	2.10	23	109	83.4	2.10
F5 (**)	554	605	N/A	-	-	-	11	282	53.4	5.40	30	231	61.8	4.40
F6	579	571	~1	151	73.6	2.90	7	130	77.2	2.50	23	110	80.7	2.10
F7	512	506	~1	125	75.3	2.40	15	139	72.5	2.70	23	119	76.5	2.30
F8(#)	518	493	~1	106	78.5	2.04	4	86	82.5	1.65	8	54	89.1	1.04

Test Number (*)	U Concentration (mg/kg)			(E)				(F)		
	Dry Feed Soil	Soil After Contact With H2O	Reaction Time (Recirc) (min)	U Conc. in Treated Soil (mg/kg)	PCRE (%)	TSQI	Reaction Time (Recirc + Filtration) (min)	U Conc. in Treated Soil (mg/kg) (***)	PCRE (%)	TSQI
F1	498	546	35	492	9.9	9.50	35 + N/A = 35	492	9.9	9.50
F2	581	561	65	N/A	-	-	65 + 175 = 240	205	63.5	3.90
F3	606	728	60	174	76.1	3.35	60 + 145 = 205	85	88.3	1.60
F4	529	658	38	97	85.3	1.87	38 + 47 = 85	47	92.8	0.91
F5 (**)	554	605	40	221	63.5	4.25	40 + 796 = 836	199	67.1	3.83
F6	579	571	38	91	84.1	1.75	38 + 45 = 83	49	91.4	0.94
F7	512	512	38	130	74.6	2.50	38 + 40 = 78	45	91.1	0.87
F8(#)	518	493	10.0	38.00	92.20	0.7	10 + 41 = 51	97	80.3	1.87

Note: (***): Concentration reported is an average of two analysis results for two separate soil samples
PCRE: Percent Contaminant Removal Efficiency
TSQI: Treated Soil Quality Index = (Final uranium concentration (mg/kg)) / (52 mg/kg (target))
(*): See Table B.28 for test conditions
(**): Test F5 using 0.2 mol/L sodium carbonate and 0.2 mol/L sodium bicarbonate as leachant
(#) : single-pass experiment, no circulation

Table B.31: Pilot-Scale Fernald Soil Leaching with Water, H2SO4 and KMnO4 - Test Conditions and Results

Task Number: F4		
Volume of Water (L)	360	
Weight of Soil (kg)	30.79	
L/S Ratio	11.7	
Uranium Conc. (mg/kg)	Analysis#1	532
	Analysis#2	527
Mean Conc. (mg/kg)		529.5

Process Data:	Time -->	0 min	1 min	8 min	23 min	38 min	Treated
Process Flow Rate (L/min)	40						
Wt. of H2SO4 (kg) (95.5%)	9.2	mol/L -->	0.25				
Wt. of KMnO4 (kg)	0.9	g/g -->	0.03				
Temperature (C)	39	39	39.5	39	39.5	39.5	
pH		7.9	1.1	0.8	0.8	0.7	
ORP (mV)		169	1141	1138	573	583	
Eh (mV)		369	1341	1338	773	783	
Ultrasonic Frequency	30 kHz						
Ultrasonic Power (W)		0	713	713	713	713	
Energy Applied (kJ/L)		0	0.24	0.95	2.73	4.52	
Uranium Conc. (mg/kg)	Analysis#1	672	118	111	103	90.6	47.4
	Analysis#2	644	140	113	115	103	47.1
Mean (mg/kg)		658	129	112	109	96.8	47.25
% Removal (%)			80.40	82.98	83.43	85.29	92.82

Wt. of Wet Cake (kg)	36.9	Filter-Aid Type: 800S	
Wt. of Filter-Aid (kg)	1.2	Loading Period: 10 min	
Moisture Content (%)	21.0	Filtering Period: 27 min	
Wt. of Treated Soil (kg)	27.9	Washing Period: 10 min	
% Soil Loss (%)	9.3	Air Dry: Yes	

Table B.32: Pilot-Scale Fernald Soil Leaching with Water, H2SO4 and KMnO4 - Test Conditions and Results

Task Number: F6		
Volume of Water (L)	390	
Weight of Soil (kg)	30.41	
L/S Ratio	12.8	
Uranium Conc. (mg/kg)	Analysis#1	583
	Analysis#2	574
Mean Conc. (mg/kg)		578.5

Process Data:	Time -->	0 min	1 min	8 min	23 min	38 min	Treated
Process Flow Rate (L/min)	40						
Wt. of H2SO4 (kg) (95.5%)	9.21	mol/L -->	0.23				
Wt. of KMnO4 (kg)	0.9003	g/g -->	0.03				
Temperature (C)		35.4	39.6	39.9	39.2	38.9	
pH		8.1	0.9	0.8	0.8	0.8	
ORP (mV)		103	1139	1145	792	735	
Eh (mV)		303	1339	1345	992	935	
Ultrasonic Frequency	30 kHz						
Ultrasonic Power (W)		0	0	0	0	0	
Energy Applied (kJ/L)		0	0.00	0.00	0.00	0.00	
Uranium Conc. (mg/kg)	Analysis#1	572	149	131	109	91.4	48
	Analysis#2	569	153	129	110	90.3	49.6
Mean (mg/kg)		570.5	151	130	109.5	90.85	48.8
% Removal (%)			73.53	77.21	80.81	84.08	91.45

Wt. of Wet Cake (kg)	40.4	Filter-Aid Type: 800S	
Wt. of Filter-Aid (kg)	2.0	Loading Period: 5 min	
Moisture Content (%)	27.1	Filtering Period: 30 min	
Wt. of Treated Soil (kg)	27.5	Washing Period: 10 min	
% Soil Loss (%)	9.7	Air Dry: Yes	

Table B.33: Summary of Pilot-Scale Fernald Incinerator Soil Leachate Treatment Results

Test Conditions

Test Number	Soil Leaching Test No.	Feed Volume (L)	Chemical Wt. (kg)	Dosage of H2O2 (mL/L)	Dosage of Fe+3 (mg/kg)	Mixing Method	Mixing Time (min)	Mean Temp (C)	Average pH	Average emf (mV)	US Power Input (W)	Wt. of Dry Waste (kg)	Volume Reduction Factor
FL2	F2	410	Ca(OH)2 3	4.90	97.6	Mech/Pump	30	23.1	11.19	199.6	0	8.70	61
FL3	F3	420	NaOH 3.19	4.80	95.2	USF/Pump	30	25.5	10.21	334.9	713	1.00	546
FL4	F4	475	NaOH 13.2	4.70	0.0	USF/Pump	0.07	28.2	10.70	449.4	713	3.50	176
FL6	F6	475	Mg(OH)2 7.14	5.00	100.0	Mech/Pump	30	21.3	7.81	435.2	0/713	1.80	343
FL7	F7	600	NaOH 7.2	5.00	0.0	USF/Pump	0.07	21.5	11.00	250	713	3.32	235
FL8	F8	475	NaOH 2.3	5.00	0.0	USF/Pump	0.07	28.3	10.50	406.2	713	1.99	310

Test Results

Test Number	Soil Leaching Test No.	U			Al			Ca			Fe			Mn			Pb			SO4			TDS		
		(mg/kg)		PCRE (%)	(mg/kg)		PCRE (%)	(mg/kg)		PCRE (%)	(mg/kg)		PCRE (%)	(mg/kg)		PCRE (%)	(mg/kg)		PCRE (%)	(mg/kg)		PCRE (%)	(mg/kg)		PCRE (%)
		Feed	Treated		Feed	Treated		Feed	Treated		Feed	Treated		Feed	Treated		Feed	Treated		Feed	Treated		Feed	Treated	
FL2	F2	33.2	0.217	99.3	85.2	1.5	98.2	482	735	-52.5	123	1.09	99.1	14.5	0.201	98.6	0.58	<0.025	>95.7	8750	1380	84.2	7530	2850	62.2
FL3	F3	33	0.288	99.1	73.3	9.11	87.6	512	316	38.3	126	1.5	98.8	11.9	0.159	98.7	0.58	<0.025	>95.7	9220	7710	16.4	4850	12000	-147.4
FL4	F4	28.7	0.674	97.7	91.3	8.65	90.5	388	274	29.4	141	0.511	99.6	107	0.407	99.6	0.129	<0.025	>80.6	18600	13900	25.3	20700	22200	-7.2
FL6	F6	28.1	0.632	97.8	97.8	0.3	99.7	443	352	20.5	164	0.19	99.9	120	50.2	58.2	0.157	<0.025	>84.1	16700	14700	12.0	19300	24900	-29.0
FL7	F7	20.6	0.165	99.2	84.8	28.1	66.9	653	125	80.9	116	0.334	99.7	95.9	0.253	99.7	0.096	0.037	61.5	14300	12700	11.2	17400	20200	-16.1
FL8	F8	35	0.743	97.9	58.2	9.49	83.7	321	211	34.3	14.5	0.299	97.9	46.9	0.817	98.3	<0.025	<0.025		5310	4300	19.0	4740	7050	-48.7

Note: USF: Mixing using Ultrasonic Liquid Processor
PCRE: *Percent Contaminant Removal Efficiency*
TDS: Total Dissolved solids
H2O2: 30 wt.% solution in water

Table B.34: Fernald Soil Pilot-Scale Leachate Treatment Results

Task Number: FL3

Feed Data:

Volume of Leachate (L)	420

	Sample No:	M884/5	M886/7	M888/9	M890/1	M892/3	M894/5	M896/7
Process Data:	Time -->	Leachate	0 min	1 min	10 min	20 min	30 min	Composite
Process Flow Rate (L/min)	25	(before					(from	
Wt. of NaOH (kg)	3.19	washing)					Press)	
Wt of Fe+3 (kg)	0.04		= ppm -->	95.2				
Vol. of 30% H2O2 (L)	2		= mL/L --	4.8				
Temperature (C)			22.6	26.3	26.3	27.1	25.2	
pH			1.25	10.92	9.93	10.01	9.97	
ORP (mV)			561.1	235.8	105.3	95.4	103.2	
emf (mV)			761.1	435.8	305.3	295.4	303.2	
Ultrasonic Frequency	30 kHz							
Ultrasonic Power (W)			0	713	713	713	713	713
Energy Applied (kJ/L)			0	1.71	1.71	1.71	1.71	1.71
Uranium Conc. (mg/kg)		34.1	33	1.65	0.188	0.4	0.229	0.288
% Removal (%)				95.00	99.43	98.79	99.31	99.13
TDS Conc. (mg/kg)		6560	4850.00	13000.00	13700.00	13600.00	12500.00	12000.00
% Removal (%)				-168.04	-182.47	-180.41	-157.73	-147.42
SO4 Conc. (mg/kg)		10200	9220.00	8330.00	8740.00	8550.00	8090.00	7710.00
% Removal (%)				9.65	5.21	7.27	12.26	16.38
Al Conc. (mg/kg)		75.2	73.30	14.50	8.40	10.20	8.90	9.11
% Removal (%)				80.22	88.54	86.08	87.86	87.57
Ca Conc. (mg/kg)		545	512.00	357.00	348.00	354.00	326.00	316.00
% Removal (%)				30.27	32.03	30.86	36.33	38.28
Fe Conc. (mg/kg)		96.2	126.00	7.58	0.773	2.21	1.15	1.50
% Removal (%)				93.98	99.39	98.25	99.09	98.81
Mn Conc. (mg/kg)		10.8	11.90	0.383	0.154	0.207	0.130	0.159
% Removal (%)				96.78	98.71	98.26	98.91	98.66
Pb Conc. (mg/kg)		0.534	0.58	<0.025	<0.025	0.03	0.04	<0.025
% Removal (%)				>95.7	>95.7	94.50	92.96	>95.7
Wt. of Wet Cake (kg)	9.0		Filter-Aid Type: 800S					
Wt. of Filter-Aid (kg)	1.9		Loading Period: 5 min					
Moisture Content (%)	67.5		Filtering Period: 30 min					
Wt. of Dried Waste (kg)	2.9		Washing Period: 0 min					
g/L Ratio (g/L)	6.9		Air Dry: Yes					

Table B.35: Pilot-Scale Fernald Soil Leachate Treatment Results

Task Number: FL7

Feed Data:

Volume of Leachate (L)	600

	Sample No:	M1011	M1013	M1015	M1017	M1019	M1021	M1023	M1025	M1027	M1029
Process Data:		Leachate	Feed	Feed	Treated Water						
Process Flow Rate (L/min)	4.5	(before washing)									
Wt. of NaOH (kg)	7.2										
Wt of Fe+3 (kg)	0		= ppm -->	0.0							
Vol. of 30% H2O2 (L)	3		= mL/L -->	5.0							
Temperature (C)			21.3	21.3	22.2	22.9	23.5	29.7	28	27.3	26
pH			1.1	1.06	12.88	12.73	12.72	12.4	12.22	12.08	11.97
ORP (mV)			559.7	561	-60	-60	-42.1	-40.7	-18.7	1.5	-22.3
Eh (mV)			759.7	761	140	140	157.9	159.3	181.3	201.5	177.7
Ultrasonic Frequency	30 kHz										
Ultrasonic Power (W)			0	0	713	713	713	713	713	713	713
Energy Applied (kJ/L)			0	0	9.5	9.5	9.5	9.5	9.5	9.5	9.5
Uranium Conc. (mg/kg)		24.2	20.6	18.2	0.04	0.0592	0.105	0.117	0.145	0.284	0.165
% Removal (%)					99.81	99.71	99.49	99.43	99.30	98.62	99.20
TDS Conc. (mg/kg)		20800	17400.00	12200.00	17600.00	18700.00	18600.00	19600.00	19700.00	20200.00	20100.00
% Removal (%)					-1.15	-7.47	-6.90	-12.64	-13.22	-16.09	-15.52
SO4 Conc. (mg/kg)		18000	14300.00	14200.00	6710.00	8580.00	9250.00	10700.00	11600.00	12000.00	12200.00
% Removal (%)					53.08	40.00	35.31	25.17	18.88	16.08	14.69
Al Conc. (mg/kg)		93	84.80	83.30	19.40	23.30	24.50	27.50	27.80	29.30	28.10
% Removal (%)					77.12	72.52	71.11	67.57	67.22	65.45	66.86
Ca Conc. (mg/kg)		384	653.00	504.00	42.40	56.80	61.70	76.40	96.20	113.00	125.00
% Removal (%)					93.51	91.30	90.55	88.30	85.27	82.70	80.86
Fe Conc. (mg/kg)		117	116.00	114.00	0.168	0.120	0.170	0.173	0.343	0.952	0.334
% Removal (%)					99.86	99.90	99.85	99.85	99.70	99.18	99.71
Mn Conc. (mg/kg)		95	95.90	96.900	0.063	0.055	0.107	0.114	0.257	0.784	0.253
% Removal (%)					99.93	99.94	99.89	99.88	99.73	99.18	99.74
Pb Conc. (mg/kg)		0.079	0.096	0.054	<0.025	<0.025	<0.025	<0.025	0.035	<0.025	0.037
% Removal (%)					>73.96	>73.96	>73.96	>95.7	63.54	>73.96	61.46
Wt. of Wet Cake (kg)	10.580		Filter-Aid Type: 800S								
Wt. of Filter-Aid (kg)	1.020		Loading Period: 5 min								
Moisture Content (%)	59.000		Filtering Period: 132 min								
Wt. of Dried Waste (kg)	4.338		Washing Period: 0 min								
g/L Ratio (g/L)	7.230		Air Dry: Yes								

Note: Treated water samples were taken from the filterpress sampling port.
The total filtrate time was 132 min.

Table B.36: Amount of Secondary Waste Generated from Chalk River Chemical Pit Soil Leachate Treatment by Chemical Precipitation/Sorption

Leachate pH	Treatment pH	Concentration of Contaminants in Leachate			Precipitant/ Co-Precipitant	Mass of Secondary Waste (g/L of Leachate Treated) Dry Weight Basis Pilot-scale (*)	Concentration of Contaminant in Treated Water			TDS	Mass of Secondary Waste Generated per ton of soil treated (lb)	Secondary Waste (dry) Generated to Soil Treated (%)	Estimated Total Activity in Secondary Waste (pCi/lb)
		U (ug/L)	Sr-90 (pCi/L)	Gross Gamma (pCi/L)			U (ug/L)	Sr-90 (pCi/L)	Gross Gamma (pCi/L)	(mg/L)			
HCl Leachate													
1.8	11.5	22.5	1.6E+04	< 2.7	Lime (2.1 g/L) Soda (3.9 g/L)	3	3.3	265	< 2.7	4500	160	8	2.3E+06
1.5	10.5	297	2.5E+04	< 2.7	Lime (3.4 g/L) Chabazite (0.25 g/L) Soda (12.8 g/L)	5.4	40	435 (265)	< 2.7	4800	178	8.9	2E+06
2.0	11.3	888	3.8E+04	<4.0	Lime (1.69 g/L) Soda (5.0g/L) Chabazite (0.25 g/L) MnO2 (0.03 g/L)	4.3	357	247	<2.7	4090	100	5.5	4.00E+06

Note: Sr-90 Data in parantheses represent solid-liquid separation by microfiltration and other data by plate-and-frame filter pressing.
Soil leaching was performed using a soil to leachant ratio of 1 to 10.
(*) About 1.2 kg of filter-aid was used per batch of leachate treatment. This amount was added based on the filter area of the filter press. In practice, the actual amount required will be significantly lower (based on the filter-aid to precipitate ratio) and therefore, the amount of filter-aid used in the tests is not included in the secondary waste quantity.

Table B.37: Summary of Dynamic Leach Test Results

Sludge to Cement Ratio (by Weight)	Waste Solid : Cement: Water Ratio (by Dry Wright)	Sample Number	Leachability Index	99.9% Confidence Range	Correlation Coefficient
1 : 1 (Sludge contained 70% water)	1 : 3.33 : 2.54	^{90}Sr			
		CP2	10.7	10.5 - 10.9	-0.68
		CP5	10.7	10.5 - 10.9	-0.68
		CP9	10.8	10.6 - 11.0	-0.68
		Mean	10.7		
		Variance	0.12		
		^{60}Co			
		CP2	12.9	12.6 - 13.2	0.58
		CP5	12.8	12.5 - 13.1	0.58
		CP9	12.8	12.5 - 13.1	0.58
		Mean	12.8		
		Variance	0.12		
		^{137}Cs			
		CP2	12.3	11.5 - 13.1	0.08
		CP5	12.0	11.2 - 12.8	0.08
		CP9	12.4	11.6 - 13.2	0.08
		Mean	12.2		
		Variance	0.42		
		^{106}Ru			
		CP2	9.2	8.9 - 9.5	-0.01
		CP5	9.2	8.9 - 9.5	0.86
		CP9	9.2	8.9 - 9.5	0.86
		Mean	9.2		
		Variance	0.0		
		^{241}Am			
		CP2	10.9	10.6 - 11.2	0.86
		CP5	10.8	10.0 - 11.6	0.86
		CP9	10.9	10.0 - 11.6	0.86
		Mean	10.9		
		Variance	0.12		

Table B.38: Compressive Strength of Cemented Waste Form

Sample Number	Compressive Strength (psi)
CP-1	1,487
CP-3	2,045
CP-4	2,529
CP-7	2,581
CP-11	1,776
Mean	2,083
Variance	847.6

Table B.39: Amount of Secondary Waste Generated from Fernald Incinerator Area Soil Leachate Treatment by Chemical Precipitation/Sorption

Leachate pH	Initial Conc. of Uranium in Leachate (mg/L)	Treatment pH	Precipitant/ Co-Precipitant	Mass of dry secondary waste (g/L of Leachate Treated)	Uranium Conc. in Treated Leachate (mg/L)	Treated Leachate		Mass of dry secondary waste generated per ton of soil treated (lb)	Number of secondary waste drums based on 60% average moisture in wet cake	Secondary waste (dry) Generated to soil treated (%)	Estimated uranium Conc. in secondary waste (dry) (%)
				Pilot-scale		TDS (mg/L)	SO4 (mg/L)				
H_2SO_4 Leachate											
1.6	35	11	Lime (7.5 g/L) H_2O_2 (1.5 g/L) Fe 3+ (0.1 g/L)	21.22	0.04 to 0.22	2850	1380	580	2.4	29	0.16
1.6	34.1	10	NaOH (7.6 g/L) H_2O_2 (1.5 g/L) Fe 3+ (0.1 g/L)	2.38	0.2 to 0.28	12000	7710	67	0.28	3.4	1.37
1.1	25.4	8	$Mg(OH)_2$ (15 g/L) H_2O_2 (1.5 g/L) Fe 3+ (0.1 g/L)	3.79	0.2 to 0.63	24900	14700	118	0.49	5.9	0.73
1.1	20.6	12	NaOH (12g/L) H_2O_2 (1.5 g/L)	5.53	0.04 to 0.17	20200	12700	221	0.92	11	0.37

Note: Soil leaching was performed using soil to leachant ratio of 1 to 10.
Mass of secondary waste excludes mass of filter-aid added.
1 ton = 2000 lb = 908 kg
1 drum = 600 lb wet cake

Table B.40: Summary of Material Balance Calculations for a 20 tph Plant

Stream	Feed	Water1	CH1A	CH1B	SL1F	SL1C (Dry Wt.)	Water2 Wash	LTE	CH3A	CH3B	SL3F	SL3C (Dry Wt.)
Mass Flow Rate (kg/h)	18160.0	181600.0	4449.2	544.8	188228.4	16525.6	30000.0	218228.4	2618.7	1091.1	220407.7	1530.5
Species	(Solid)		H2SO4	KMn04	(Liquid)	(Solid)			NaOH	H2O2(30%)		
TSS (mg/kg)	1000000.00	1.00			8683.15	1000010.00	1.00	7604.39			3.74	1083666.00
TDS (mg/kg)	0.00	12.00			23009.85	0.00	12.00	20152.33			26600.13	26600.13
Uranium (mg/kg)	550.00	0.00			48.82	48.35	0.00	42.75			0.29	6053.10
Iron (mg/kg)	21500.00	3.00			415.44	18927.47	3.00	364.19			1.79	51667.10
Calcium (mg/kg)	12000.00	3.00			928.51	2643.96	3.00	813.51			479.95	46875.02
Lead (mg/kg)	35.00	1.00			0.87	39.56	1.00	0.88			0.04	119.87
Manganese (mg/kg)	925.00	2.00		347688.41	109.75	11250.65	2.00	96.36			1.23	13561.62
Aluminum (mg/kg)	13000.00	1.00			188.28	12152.20	1.00	165.01			16.23	21189.86
Sulphate (mg/kg)	15.00	1.00	979591.84		21304.68	21101.10	1.00	18657.67			16511.21	282525.15
Sodium (mg/kg)	30.00	1.00			1.93	21.98	1.00	1.81	575000.00		6107.80	104511.25

<u>Note:</u>

(1) Chemical Addition: [sulphuric acid] = 0.025 mol/L; [potassium permanganate] = 0.03 kg/kg; [sodium hydroxide] = 0.012 kg/L and [30% hydogen peroxide] = 5 mL/L.

(2) Soil Dissolution in Soil Leaching Step: 9%.

(3) Contaminant Removal Efficiencies (%) for Soil Leaching:
TSS = 9%; TDS = 100%; U = 92%; Fe = 20%; Ca = 80%; Pb = 20%; Mn = 10%; Al = 15 %; SO4 = 92% and Na = 50%.

(4) Contaminant Removal Efficiencies (%) for Soil Leachate Treatment:
TSS = 99.9%; TDS = 0%; U = 99.3%; Fe = 99.5%; Ca = 40%; Pb = 95%; Mn = 98.7%; Al = 90 %; SO4 = 10% and Na = 10%.

Stream designations are given in Figure A.39:

Feed : Contaminated soil feed
Water1 : Water for making up the leachant solution
CH1A : Concentrated sulfuric acid
CH1B : Potassium permanganate
SL1F : Soil leachate
SL1C : Treated soil
Water2 : Wash water
LTE : Combined soil leachate and wash water
CH3A : Sodium carbonate
CH3B : Hydrogen peroxide
SL3F : Treated water
SL3C : Secondary waste

Table B.41: A Summary of Estimated Costs of Soil Leaching Plant

Plant Capacity:	20 ton/h
Plant Life :	5 years

			Cost (US$)
I. Capital Cost			
1. Equipment, [E]			$4,382,200
2. Installation [0.15 x E]			$657,300
3. Instrumentation [0.08 x E]			$350,600
4. Piping [0.05 x E]			$219,100
5. Electrical [0.08 x E]			$350,600
6. Building [0.35 x E]			$1,533,900
7. Service Facility [0.1 x E]			$438,200
8. Yard Improvements [0.03 x E]			$131,500
9. Land			N/A
10. Total Direct Cost (TD), [1 to 9]			**$8,063,400**
11. Engineering [0.1 x TD]			$806,300
12. Project Management [0.1 x TD]			$806,300
13. Contingency [0.15 x TD]			$1,209,500
14. Total Indirect Cost (TI), [11 to 13]			**$2,822,100**
15. Fixed Capital [10 + 14]			**$10,885,500**
II. Operating Cost			
16. Chemicals/Reagents			**$11,624,700**
17. Total Labour Costs (L)	$32 / h	35121	**$1,123,900**
Utilities			
18. Process energy	$0.06 / kWh		$5,164,000
19. Potable Water	$2 / 150 gal		$5,172,500
20. Other (steam, compressed air)			$437,300
21. Total Utilities (U), [18 to 20]			**$10,773,800**
22. Maintenance & Repair (M)			$186,300
23. Laboratory Charges [0.1 x L]			$112,400
24. Operating Supplies [0.3 x M]			$55,900
25. Patents and Royalties			N/A
26. Disposal Cost			$0
27. Direct Operating Cost [16+17+21+22 to 26]			**$23,877,000**
28. Depreciation			$788,800
29. Fixed Charge for Permit and Regulatory			$200,000
30. Fixed Charge for Demobilization			$200,000
31. Local Taxes [0.02 x (TD+TI)]			$217,700
32. Insurance [0.02 x (TD+TI)]			$217,700
33. Rent			N/A
34. Plant-overhead Cost [0.5 x (L+M)]			$655,000
35. Fixed Charges [28 to 34]			**$2,279,200**
36. Adminstration [0.15 x (L+M)]			$196,500
37. R&D			N/A
38. Financing [0 x (L+M)]			$0
39. General Expenses [36 to 38]			**$196,500**
40. Total Operating Cost [27+ 35 +39]			**$26,352,700**

Total leachate treated	143,994 tons	
	Total	Direct
Operating Cost Per Ton of Soil	$183.01	$165.82
Operating Cost Per Day	$76,830	$69,612

Table B.42: A Summary of Estimated Costs of Leachate Treatment Plant

Plant Capacity:	1070 gpm
Plant Life :	5 years

			Cost (US$)	
I. Capital Cost				
1. Equipment, [E]			$4,438,500	
2. Installation [0.1 x E]			$443,900	
3. Instrumentation [0.05 x E]			$221,900	
4. Piping [0.05 x E]			$221,900	
5. Electrical [0.05 x E]			$221,900	Note: Items 6 to 8 reflect only an arbitrary allocation of a portion of the building related cost. The total building related cost will be the sum of those for the soil leaching and leachate treatment plants
6. Building [0.1 x E]			$443,900	
7. Service Facility [0.02 x E]			$88,800	
8. Yard Improvements [0.02 x E]			$88,800	
9. Land			N/A	
10. Total Direct Cost (TD), [1 to 9]			**$6,169,600**	
11. Engineering [0.1 x TD]			$617,000	
12. Project Management [0.1 x TD]			$617,000	
13. Contingency [0.15 x TD]			$925,400	
14. Total Indirect Cost (TI), [11 to 13]			**$2,159,400**	
15. Fixed Capital [10 + 14]			**$8,329,000**	
II. Operating Cost				
16. Chemicals/Reagents			**$16,957,200**	
17. Total Labour Costs (L)	$32 / h	35696	**$1,142,300**	
Utilities				
18. Process energy	$0.06 / kWh		$548,000	
19. Potable Water	$2 / 150 gal		$253,600	
20. Other (steam, compressed air)			$131,200	
21. Total Utilities (U), [18 to 20]			**$932,800**	
22. Maintenance & Repair (M)			$173,400	
23. Laboratory Charges [0.1 x L]			$114,200	
24. Operating Supplies [0.3 x M]			$52,000	
25. Patents and Royalties			N/A	
26. Disposal Cost			$1,281,400	
27. Direct Operating Cost [16+17+21+22 to 26]			**$20,653,300**	
28. Depreciation			$798,900	
29. Fixed Charge for Permit and Regulatory	[Items 29 and 30 are included in the soil leaching process]			
30. Fixed Charge for Demobilization				
31. Local Taxes [0.02 x (TD+TI)]			$166,600	
32. Insurance [0.02 x (TD+TI)]			$166,600	
33. Rent			N/A	
34. Plant-overhead Cost	Same as item 29			
35. Fixed Charges [28 to 34]			**$1,132,100**	
36. Adminstration [0 x (L+M)]	Same as item 29			
37. R&D			N/A	
38. Financing [0 x (L+M)]	Same as item 29			
39. General Expenses [36 to 38]			**$0**	
40. Total Operating Cost [27+ 35 +39]			**$21,785,400**	

	Total	Direct
Total leachate treated	462,222,281 gal	
Operating Cost Per 1000 gal	$47.13	$41.91
Operating Cost Per Day	$63,514	$56,478