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Mound-ACT*DE*CON^{SM} Feasibility Study,[†] Phase II: Final Report

Argonne National Laboratory,
Selective Environmental Technologies, Inc.,
Bradtec Ltd., and
RUST Federal Services, Inc.

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MASTER

[†] *Formerly Mound-Bradtec Feasibility Study.*

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Preface

This document reports on the activities and findings of Phase II of the Mound-ACT*DE*CON^{SM} (formerly Mound-Bradtec) Feasibility Study. The research activity has been performed, according to the original scope of work, by Bradtec Ltd., Bristol, U.K.; Selective Environmental Technologies, Inc. (SELENTEC), Atlanta, Ga.; Argonne National Laboratory, Argonne, Ill.; and RUST Federal Services, Inc., Golden, Colo. In May 1995, Bradtec-U.S., Inc. changed its name to SELENTEC. The new name has been adopted throughout this report to identify Bradtec-U.S., Inc.

Each author reported on his/her work in a separate Task Report. Argonne has assembled the separate Task Reports into one document. In order to allow recognition of each investigator's work, the original structure given by each author was maintained, but the text, tables, and figures were formatted in a uniform style.

Chapter I reports the findings of Bradtec Ltd. and SELENTEC under Tasks 1, 2, 4, 5, 6, 8, 9, 10, and 11 of the Scope of Work. Chapter II discusses the results of Plutonium Mobility Studies (Task 3) performed by Argonne National Laboratory. Chapter III, Waste Stabilization Study (Task 7), and Chapter IV, Dewatering Study (Task 13), report on RUST's work. Technology development problems encountered while pursuing work on Tasks 4, 5, and 6 prevented the samples of magnetic particles to be used for the Task 7 laboratory studies from being obtained. Thus, the Task 7 report documents the preliminary work done on the subject of waste stabilization and related investigations but contains no laboratory data.

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Executive Summary

The U.S. Department of Energy and the U.S. Environmental Protection Agency have identified contaminated sediment as a major problem at several U.S. Government sites. Mound, a former plutonium-processing facility in Miamisburg, Ohio, is one such site, with an estimated one million cubic feet of plutonium-contaminated soil/sediment in the Miami-Erie Canal. The technology being evaluated for the remediation of the low-level plutonium-238 contamination of the sediment at the Mound site involves two processes: washing the sediments with ACT*DE*CON^{SM} solution to dissolve the contaminant, followed by extraction of the solution and processing with the MAG*SEP^{SM} process to concentrate the contaminant and allow reuse of the ACT*DE*CON^{SM} solution. The processes are being optimized for pilot-scale and field demonstration. Phase II of the project primarily involved identification at the laboratory scale of the optimal ACT*DE*CON^{SM} formulation, identification of the ion-exchanger and MAG*SEP^{SM} particles, verification of the plutonium mobility in the treated soil, and evaluation of other process parameters according to the following series of tasks:

Task 1	Optimization of the ACT*DE*CON^{SM} Formulation for Spiked Mound Sediment
Task 2	Evaluation of the Dissolution of Nonhazardous Minerals
Task 3	Plutonium Mobility Studies in Soil/Sediment Treated with ACT*DE*CON^{SM}
Task 4	Ion-Exchange Material Studies
Task 5	Magnetic Particle Optimization Studies
Task 6	Magnetic Particle Regeneration Studies
Task 7	Waste Stabilization Study
Task 8/10	Laboratory-Scale Integration Test with Mound Site Sediment
Task 9	Laboratory-Scale Dissolution Tests with Mound Site Sediment
Task 11	Commercial-Scale Magnetic Particle Recovery
Task 12	Final Report
(Task 13)	Dewatering Study of ACT*DE*CON^{SM}-Treated Sediments from the Mound Site
(Task 14)	Plutonium Speciation

With the use of artificially contaminated Mound sediment, eleven experimental ACT*DE*CON^{SM} formulations were examined under Task 1 for ability to reduce the plutonium contamination to an acceptable level, by using the lowest chemical loading. A successful formulation was found, which is referred to as the "optimized formulation."

In order to minimize the volume of secondary waste that will require treatment and disposal following application of the ACT*DE*CON^{SM} process, the dissolution of the most abundant elements present in the sediment was evaluated (Task 2). This evaluation was performed on the treated sediment after contact with the optimized formulation and also, later in the program, after contact with the "modified" ACT*DE*CON^{SM} formulation. In both evaluations, the percent removal of nonhazardous minerals was approximately 2%; this value was less than the target maximum of 10%.

Plutonium mobility studies (Task 3) that used Mound-collected rainwater and contaminated Mound sediment were conducted. The mobility of the residual plutonium after treatment of the soil with the modified ACT*DE*CON^{SM} solution was evaluated and compared with the plutonium mobility of untreated soil (considered, for the present time, as the reference status not to be worsened) and with treated soil amended with a conventional fertilization. Results showed that after 90 days of incubation from the end of the treatment, plutonium in treated soil, in treated/fertilized soil, and in untreated soil had the same level of mobility in rainwater, whereas after shorter incubation periods, the plutonium in the treated soil was less mobile than the plutonium in the other two soils.

In the ion-exchange studies (Tasks 4-6), the initial objectives were to (1) identify a suitable ion-exchange material from which to prepare MAG*SEP^{SM} particles, (2) optimize the MAG*SEP^{SM} particle contact time and solution-to-particle ratio, and (3) evaluate the regeneration conditions of the particles. The ion-exchange material identified at an early stage of the program was ineffective in exchanging the plutonium in the ACT*DE*CON^{SM} at the chemical conditions required to decontaminate the weathered Mound sediment. As a result, Tasks 4-6 were merged, and emphasis was placed on the identification of the chemical form of the plutonium in spent ACT*DE*CON^{SM} solution that had been used to treat weathered sediment. This investigation indicated that the plutonium could be removed from spent ACT*DE*CON^{SM} with an anion exchange resin, but not in a manner selective for plutonium, and therefore, not in a feasible way. A speciation study using DEAE cellulose suggested that more than 80% of the plutonium was associated with the ACT*DE*CON^{SM} chelant and less than 20% was associated with the sediment organic material (humic, fulvic acids).

An initial evaluation of the full process application was performed under Task 8/10. A system that simulated the conditions of field application was designed and constructed. Processing noncontaminated sediment through the system demonstrated the difficulties that will be incurred with an in-situ approach. Due to the high percentage of silt and clay in the sediment, percolation of the ACT*DE*CON^{SM} solution through the sediment was impractical. Investigation into alternative means of solid/liquid separation is required, prior to a pilot-scale engineering effort.

Once the optimized ACT*DE*CON^{SM} formulation was developed by testing on clean Mound sediment that had been artificially spiked with plutonium, the same formulation was tested (Task 9) on contaminated material from the Miami-Erie Canal. It was found that the plutonium in artificially spiked sediment, although initially thought to behave like the plutonium in Mound sediment, in fact behaved quite differently. The optimized ACT*DE*CON^{SM} formulation developed in Task 1 was not able to remove the tightly bound plutonium from the weathered, contaminated Mound sediment. Reformulation of the ACT*DE*CON^{SM} solution resulted in a "modified" solution able to decontaminate the weathered Mound sediment to an acceptable level. However, several trials with different chemicals were needed to achieve the required decontamination levels, and the final solution (called modified ACT*DE*CON^{SM}) was significantly more aggressive than the originally optimized one.

Testing of MAG*SEP^{SM} particle recovery, conducted in Task 11, demonstrated that particles were efficiently recovered from sediment slurries of up to 5% solids. Less than 0.1% of the particles were detected in the process effluent after magnetic separation. This result indicates that only one pass through a magnetic filter unit will be required to retrieve more than 99% of the particles.

Analysis of the Mound sediment showed high concentrations of magnetic and paramagnetic materials. In order to minimize the quantity of material that has to be handled as secondary waste, the magnetic and paramagnetic material will have to be removed from the process slurry before treatment with MAG*SEP^{SM}. Since no testing was performed with the MAG*SEP^{SM} system on contaminated sediment, a determination of the amount of plutonium associated with the magnetic and paramagnetic material will have to be performed. If the plutonium is adequately removed during the wash process, this material could be returned to the Miami-Erie Canal.

Two tasks were added to the scope of work during the Phase II activities, in an effort to help resolve outstanding technical issues. These two tasks (Tasks 13 and 14) dealt with preliminary evaluation of dewatering options and with speciation of the plutonium present in the Mound material.

Task 13 (formerly part of Task 3) was aimed at determining the most promising methods of dewatering the ACT*DE*CON^{SM}-treated material, in order to allow the extractant solution and entrained contaminant to be easily removed from the soil. Laboratory tests involved the use of chemical flocculants and physical additives that would improve the hydraulic parameters of the dewatering process (such as filtration time, filter cake quality, and filtrate quality). Results showed that pretreatment of the slurry with ferric chloride and lime (to be scaled up to a plate-and-frame filter-press system) reduced the dewatering time by a factor of 20-30. However, in-depth testing of the effects of the dewatering aids on the plutonium chemistry is required.

Speciation studies (Task 14), conducted as an extension of Task 9 and reported under Task 9 in Chapter I, were aimed at understanding the nature of the association of the plutonium with the various fractions of the Miami-Erie sediment; the goal was to identify the most suitable extractant. Data from sequential extractions conducted at Harwell Laboratories (United Kingdom) indicated that, in the untreated contaminated sediment, approximately 53% of the plutonium is associated with the organic material, 43% is associated with oxides, less than 2% is in readily available/exchangeable forms, and about 3% is unextractable even with strong acids (residual plutonium). After treatment with the optimized ACT*DE*CON^{SM} formulation, the soil still contained significant amounts of organic- and oxide-associated plutonium. Only treatment with the modified ACT*DE*CON^{SM} solution was able to remove a significant portion of the plutonium from these two associations.

Introduction and Scope

A portion of the abandoned Miami-Erie Canal paralleling the Greater Miami River receives the runoff and storm-water discharge from Mound Laboratory. In 1969, a low-level plutonium leak contaminated sediment as far away as 1.5 mi from the Mound site along the old canal system. An estimated one million cubic feet of sediment requires remediation. The U.S. Department of Energy's (DOE's) Office of Technology Development has funded a project by Argonne National Laboratory (ANL), Bradtec Ltd., Selective Environmental Technologies, Inc. (SELENTEC), and RUST Federal Services to investigate the use of ACT*DE*CON^{SM} and MAG*SEP^{SM} for remediation of the site.

The sediment from the Mound site has a high silt and clay content. Approximately 88% of the sediment has a diameter less than 53 µm, with 33% having less than 2 µm. Approximately 70% of the plutonium contamination is associated with the less-than-2-µm fraction. Conventional sediment washing techniques that use particle separation would generate too large a waste volume to be economically feasible.

ACT*DE*CON^{SM} is a chemical wash process that dissolves and removes heavy metals, actinides, and other radionuclides from sediment, soil, and sludges. MAG*SEP^{SM} selectively removes the contaminants from the spent ACT*DE*CON^{SM} to allow recycle of the solution. In this phase of the project, the bench-scale optimization of the ACT*DE*CON^{SM} formulation is performed and the adsorption materials for MAG*SEP^{SM} for use at the Mound site are identified.

SELENTEC and Bradtec Ltd. have developed the ACT*DE*CON^{SM} process for use in sediment washing to chemically dissolve and remove metal and radioactive contaminants.[1] The process uses oxidative carbonate chemistry[2] to dissolve the contaminant from the sediment and a chelating agent to complex and hold the contaminant in solution. MAG*SEP^{SM} is a method for removing the contamination from the wash solutions.[3] Particles with an outer adsorber coating selectively recover the dissolved contaminants and allow reuse of the ACT*DE*CON^{SM} solution. The particles have a magnetite core that permits their removal by commercially available magnetic filtration.

In the current phase of this project, a modified formulation of the ACT*DE*CON^{SM} chemistry was developed for plutonium dissolution at the Mound site. Preliminary bench-scale testing on spiked sediments produced an optimum formulation that proved to be ineffective when tested on a sample of sediment from the Mound site. Additional testing was required to modify the formulation to dissolve the "weathered" plutonium from Mound site sediment.

1 Process Description

The ACT*DE*CON^{SM} process combines established carbonate-recovery chemistry for actinide dissolution with a chelant in an oxidative environment. Contaminant recovery and solution regeneration can also be provided to produce a continuous, recirculating process for the treatment of sediments to remove strontium, cesium, technetium, radium, actinides (uranium and transuranics), barium, lead, and mercury. A variety of chemical concentration ratios can be utilized.

An oxidant is required to raise the oxidation state of the contaminant. For example, when plutonium is present in a low oxidation state (IV), the oxidant is required to raise the oxidation state to allow formation of plutonium carbonate complexes. The function of the chelant is not fully understood, but it is an important factor in the formation of soluble complexes.

Because the chemicals used are aqueous-based, a washing technique can be used for both in-situ and ex-situ treatment of sediments. The basic process consists of contaminant dissolution, contaminant recovery, and solution reconditioning.

For in-situ application, fresh ACT*DE*CON^{SM} solution is added to the sediment through a mixing device. The mixing device will have a cutting/mixing blade with solution injection capability. Several commercially available devices will be evaluated prior to field application at the Mound site to mix the ACT*DE*CON^{SM} solution and fine clay sediment. The mechanical mixing blades will uniformly blend the solution with the sediment to prevent channeling that would leave some of the sediment untreated. The expected cleaning-treatment zone in the canal is at a depth of 3-5 ft.

As the fresh ACT*DE*CON^{SM} solution contacts the contaminated sediment, plutonium is solubilized. The solution is then extracted from the treatment zone by the use of a solids separation process. The plutonium is removed from the solution by using MAG*SEP^{SM} particles. The solution can then be returned to the system for reuse. Some chemical adjustments are made, as required to maximize effectiveness, prior to reinjection of the ACT*DE*CON^{SM} solution.

MAG*SEP^{SM} is a technology that uses specially designed adsorbing particles to selectively recover contaminants in the presence of high particulate concentrations.[3,4] The particles are made of a composite consisting of magnetite and organic polymers. A polymer coating is applied to the magnetic core to give the particle durability; the coating is designed to contain a "functional group," or to bind selective adsorbing seeds to the particle. The particles can vary in size from approximately 10 to 100 μm. In testing to date, the particles are in the range of 50 μm. The low concentration of plutonium in the ACT*DE*CON^{SM} wash solution, together with the rate of diffusion of plutonium onto the particles, are the rate-limiting factors for the MAG*SEP^{SM} process. However, the probability of the plutonium reaching a particle can be enhanced by various mixing techniques. Because the adsorption process is a surface phenomenon, the plutonium is adsorbed very rapidly once it comes in contact with a particle.

The particles are recovered from the flow stream by magnetic filtration. Magnetic filter systems available from several manufacturers have flow capacities in excess of 2,000 gal/min (gpm).[5] After being recovered, the MAG*SEP^{SM} particles can be treated chemically to regenerate the adsorber, allowing recovery and concentration of the contaminants. The particles can then be reused. Alternatively, the particles can be collected and stabilized for disposal.

2 Terms and Definitions

In order to maintain consistent terminology throughout project documentation, several key terms have been defined as described below. The definitions include other terms that are sometimes used interchangeably in the proposal, contract, various procedures, and reports.

Optimum Formulation

The optimum formulation is the ACT*DE*CON^{SM} formulation utilized during the Tasks 1 and 2 testing on artificially spiked sediment. (Subsequent testing of this formulation on Mound site sediment resulted in marginal dissolution of the weathered plutonium.)

Modified Formulation

The modified formulation is the ACT*DE*CON^{SM} formulation utilized during Task 9 testing. (The modified formulation has a higher chemical concentration and uses higher temperature conditions than the optimum formulation to dissolve the plutonium in the Mound site sediment.)

Mound Site Sediment

The Mound site sediment is sediment taken from the section of the Miami-Erie Canal in Miamisburg, Ohio, that is contaminated with plutonium.

Spiked Sediment

The spiked sediment is sediment taken from a noncontaminated section of the Miami-Erie Canal that is artificially spiked with plutonium nitrate in the laboratory.

Electromagnetic Filter

The term, electromagnetic filter, refers to the commercial-scale electromagnetic filter demonstration unit manufactured by Babcock & Wilcox Nuclear Technologies (BWNT) that is used in the MAG*SEP^{SM} pilot-scale system; it may also refer to other commercial electromagnetic filter systems manufactured by BWNT. The electromagnetic filter may also be referred to as magnetic filter or EMF.

3 Scope of Testing

Phase I demonstrated that ACT*DE*CON^{SM} was able to remove plutonium contamination from artificially spiked sediment.[6] DOE, through ANL, funded a second phase of the program (Phase II) to optimize and demonstrate the ACT*DE*CON^{SM} process at the bench scale for potential full-scale application on the Mound site. The contract scope of work identified separate tasks for developing the process at the bench-scale level. The objective of each task is described below.

*Task 1 Optimization of the ACT*DE*CON^{SM} Formulation for Spiked Mound Sediment*

The objective of Task 1 was to perform a matrix of tests on spiked sediments to optimize the ACT*DE*CON^{SM} formulation. The testing was designed to determine the formulation with the lowest chemical loading that would still achieve the objective of reducing the plutonium contamination to ≤25 pCi/g. Sediment samples from a noncontaminated section of the canal were used after being artificially spiked with ^{238}Pu in a nitric acid solution (replica of original contaminant form).

Task 2 Evaluation of the Dissolution of Nonhazardous Minerals

The objective of Task 2 was to evaluate the most abundant elements present in the sediment and ascertain that less than 10% of the sediment mineral content was removed after treatment with the ACT*DE*CON^{SM} process. By reducing the quantity of minerals removed from the washed sediment, posttreatment of the sediment to enable plant growth is minimized.

*Task 3 Plutonium Mobility Studies in Soil/Sediment Treated with ACT*DE*CON^{SM}*

Task 3 was a study to be performed by ANL to determine if the sediment, following ACT*DE*CON^{SM} treatment, can still maintain plant life and to evaluate the mobility characteristics of the residual plutonium. Uncontaminated Mound sediment was prepared for this study during the work for Tasks 8/10 (Section I.4). (Due to the changing application conditions for the ACT*DE*CON^{SM} treatment, comprehensive investigation of plant regrowth has been shifted to a later phase of the program. Preliminary results are reported by ANL researchers in Chapter II of this final report.)

An additional scope of work was added to Task 3 involving the evaluation of soil additives that can be used during process application to enhance the solid/liquid separation and assist the treated sediment in supporting plant growth. This work is presented in Chapter II of this final report.

Task 4 Ion-Exchange Material Studies

The objective of Task 4 was to identify different ion-exchange materials and to select the most efficient material for the adsorption of plutonium from spent wash solutions. Various organic and inorganic adsorption materials were investigated to determine the ability of each to remove dissolved plutonium from the wash solutions.

Task 5 Magnetic Particle Optimization Studies

Task 5 involved the preparation of MAG*SEP^{SM} particles from the adsorber identified in Task 4 and the determination of the particle concentration for plutonium removal from the wash solution. The particle kinetics were also to be evaluated to determine the concentrations and contact times necessary to achieve acceptable results.

Several inorganic materials showed potential for adsorbing plutonium, but after the formulation change required for Mound site sediment, the adsorbers identified in Task 4 were unable to adsorb plutonium from spent ACT*DE*CON^{SM} solutions. Task 5 was then combined with Task 6 to identify the form of the plutonium in the spent ACT*DE*CON^{SM} solution. This study involved the investigation of the organic plutonium in solution to determine the size and type of colloid structure.

Task 6 Magnetic Particle Regeneration Studies

Task 6 was to evaluate the appropriate regeneration chemistry for the recovery and reuse of the magnetic particles. The particles prepared and tested in Task 5 were to be regenerated and reused to determine their ability to remove additional plutonium from the wash solutions. Because of the change in scope, this task was combined with Task 5.

Task 7 Waste Stabilization Study

In Task 7, the regulations governing the disposal of the waste generated from the field application of the process were evaluated. The potential waste forms from the process were to be identified and evaluated against the DOE Waste Acceptance Criteria to determine acceptable methods for disposal. Due to the change in application conditions, the waste stabilization study was shifted to a later phase of the project. A summary of preliminary work conducted on this subject as part of this phase of work is reported in Chapter III of this final report.

Task 8 Laboratory-Scale Integration Test with Mound Site Sediment

Task 8 was originally planned as a larger laboratory-scale integrated test on spiked sediment, but it was combined with Task 10 because of the differences found between spiked sediment and contaminated Mound site sediment.

Task 9 Laboratory-Scale Dissolution Tests with Mound Site Sediment

The objective of Task 9 was to demonstrate dissolution of plutonium from contaminated Mound site sediment. A sample of the sediment was shipped to the laboratory for process verification testing. During the testing it was discovered that the plutonium-contaminated sediment behaved differently than spiked sediments. The dissolution testing had to be repeated to determine the formulation that most effectively removed plutonium from Mound site sediment. A speciation analysis (see Task 14) was included in the investigation to determine how the plutonium was bound to the sediment.

Task 10 Laboratory-Scale Integration Test with Mound Site Sediment

The objective of Task 10 was to perform a larger laboratory-scale test to demonstrate the combination of the treatment process to dissolve the plutonium with the plutonium-recovery process. The regeneration and reuse of the particles for additional plutonium removal was also included in this task.

Because of the change in the ACT*DE*CON^{SM} formulation required for the Mound site sediment, the adsorbers identified in Task 4 were ineffective in removing the dissolved plutonium. The objectives of Tasks 5 and 6 were changed to identify the type of plutonium-organic species present in the ACT*DE*CON^{SM} solution. The plutonium recovery with MAG*SEP^{SM} process particle regeneration and reuse was suspended until a later phase of the project.

Task 11 Commercial-Scale Magnetic Particle Recovery

A prototype of the magnetic filtration unit was tested to demonstrate the effects of entrained sediment on the magnetic filtration process. Sediment was slurried in water at concentrations of 1%, 3%, and 5% and passed through the magnetic field at flow rates up to 20 gpm to determine the quantity of magnetic and paramagnetic material contained in the sediment. Sediment with natural magnetic and paramagnetic material removed in a pretreatment step was combined with MAG*SEP^{SM} particles to demonstrate the removal efficiency of the particles. The particles used had an adsorber coating.

Task 12 Final Report

A final report detailing the research conducted under Phase II of the program was prepared and is this document.

*Task 13 Dewatering Study of ACT*DE*CON^{SM}-Treated Sediments from the Mound Site*

The purpose of this task was to find ways to achieve an acceptable solid-liquid separation after the ACT*DE*CON^{SM} treatment. Because of the high clay and sodium content and because the treatment generates a significant amount of friction, the soil is left in a deflocculated state after plutonium extraction, and natural settling will not occur in an acceptable period of time. This task investigated the use of dewatering technologies and filter aids for the removal of the spent ACT*DE*CON^{SM} from the soil.

Task 14 Plutonium Speciation

Mound sediment was analyzed by sequential solvent extraction. The data for untreated material were compared to the data for treated material to understand the plutonium speciation and association of the plutonium species with the different fractions of the soil matrix and to determine which species were removed by the ACT*DE*CON^{SM}. (This task is an extension of Task 9 and the results are described fully under Task 9.)

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Chapter I

Report on Tasks Conducted by SELENTEC and Bradtec Ltd.

Task 1	Optimization of the ACT*DE*CON^{SM} Formulation for Spiked Mound Sediment
Task 2	Evaluation of the Dissolution of Nonhazardous Minerals
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Chapter I

Report on Tasks Conducted by SELENTEC and Bradtec Ltd. (Tasks 1, 2, 4, 5, 6, 8, 9, 10, 11)

Summary

The U.S. Department of Energy and the U.S. Environmental Protection Agency have identified contaminated sediment as a major problem at several U.S. Government sites. Mound Laboratory, a former plutonium processing facility in Miamisburg, Ohio, is one such site, with an estimated one million cubic feet of contaminated sediment. A technology consisting of two processes is being evaluated for remediation of the sediment from the Mound site, which has become contaminated with low levels of plutonium. The treatment involves washing the sediments with ACT*DE*CON^{SM} solution to dissolve the contaminant. Following extraction from the sediment, the solution is treated by the MAG*SEP^{SM} process or by evaporation to concentrate the contaminant. This technology is being optimized for pilot-scale and field demonstrations, which are planned for the future.

A modified formulation for ACT*DE*CON^{SM} has been developed that reduces the plutonium concentration to desired levels in treated Mound site sediment samples. Early work was performed on simulated sediments that had been artificially spiked with plutonium. The optimum formulation developed was not effective when applied on the "weathered" Mound site sediment. Sequential solvent extraction was used to identify how the plutonium was associated with the sediment. Analysis showed that a high percentage of the plutonium was associated with the organic and oxide fractions of the sediment. Only a small percentage was in an exchangeable form with the sediment, which was the form in the artificially spiked sediment.

Various filtration methods and filtration enhancements were examined for their potential use in the pilot-plant and field demonstrations. Because the Mound sediment contains a large fraction of silt and clay material, solid/liquid separation has become an important issue. Investigations to date have not resolved this issue.

A commercial-scale MAG*SEP^{SM} application system was used to evaluate the physical properties of sediment slurries and the effectiveness of particle separation. Magnetic filtration has been demonstrated to be an efficient method for particle removal from 1 to 5% sediment slurries.

I.1 ACT*DE*CON^{SM} Laboratory Studies (Tasks 1 and 2)

Due to the complicated and differing nature of soil and sediment chemistry and the contaminant being treated, it is necessary to study and optimize the ACT*DE*CON^{SM} process for each site. The sediment in the Miami-Erie Canal is primarily composed of clay and silt. A particle size distribution shows that approximately 88% of the sediment has a particle size smaller than 53 μm, with approximately 33% below 2 μm. The plutonium concentration has been found to be primarily associated with the smallest fraction of the sediment. Approximately 70% of the plutonium contamination is found in the less-than-2-μm fraction.[1] Figure I.1 shows a particle size distribution and the quantity of plutonium associated with each fraction. Because of the high percentage of silt and clay material, typical sediment washing techniques, which remove the small particle sediment fraction, would generate high waste volumes and would be of little benefit over "box and bury" treatment.

The effectiveness of ACT*DE*CON^{SM} in removing the plutonium was demonstrated in the laboratory and is described in the report for the proof of principle study for Phase I.[2,3]

I.1.1 Optimization of the ACT*DE*CON^{SM} Formulation

ACT*DE*CON^{SM} is an aqueous mixture of carbonate and chelating agent in an oxidizing environment at a basic pH. The wash solution can be applied under ambient conditions or at elevated temperature. By varying the chemical constituents, the formulation with the lowest chemical burden that reduces the contaminant level to acceptable levels can be determined.

In order to determine the optimum formula, a matrix of tests was performed with various concentrations of the ACT*DE*CON^{SM} chemical constituents. A matrix of eleven formulations, each with a different chemical concentration ratio, was used to establish the optimum ACT*DE*CON^{SM} formula. The criteria used to evaluate the results were (1) the reduction of the concentration of plutonium to ≤25 pCi/g and (2) minimum chemical concentration. An additional objective was to minimize the dissolution of nonhazardous minerals.

The tests were performed as batch equilibrium studies on artificially contaminated sediments. Sediment taken from a noncontaminated section of the canal was spiked to a level of 500 ± 100 pCi/g ^{238}Pu. The treatment objective was to reduce the plutonium levels in the spiked sediment to ≤25 pCi/g while dissolving less than 10% of the sediment's nonhazardous minerals.

The sediment as received was dried at 60°C for 24 h to remove the residual moisture. The dried sediment was then sieved through a 325-μm screen to remove the larger fraction of the sediment, which had been determined to have little or no plutonium contamination. The smaller

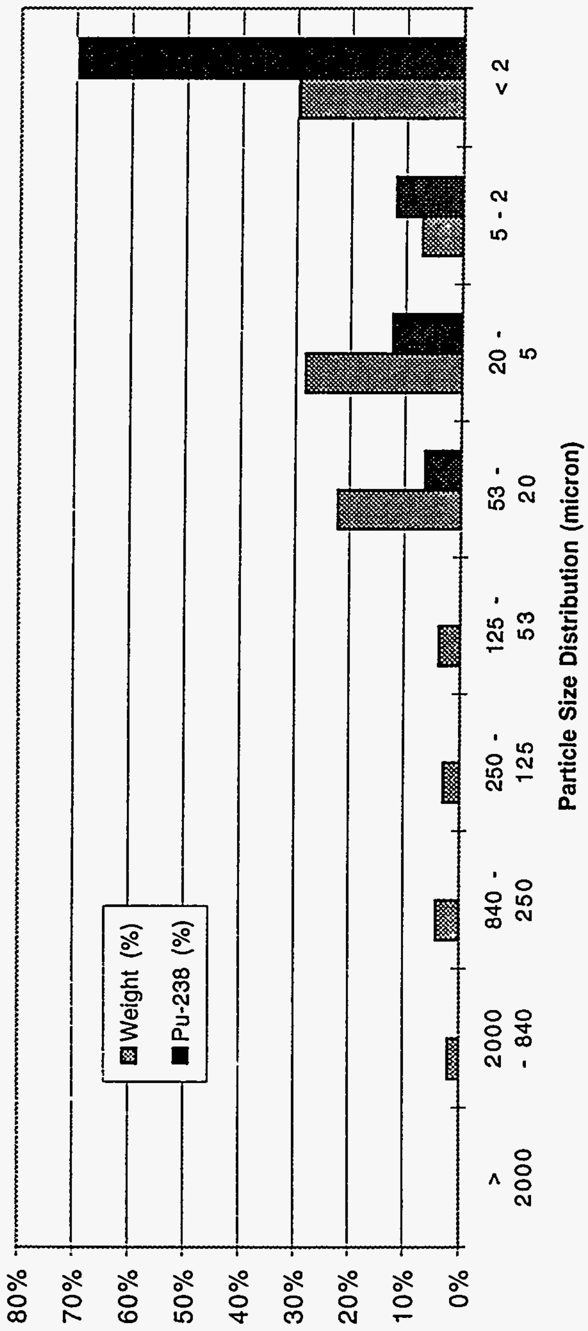

FIGURE I.1 Plutonium and Particle Size Distributions for Miami-Erie Canal Sediment (ultrasonic data) sieved fraction was spiked with ^{238}Pu in a nitric acid solution. This method was identified by Mound as a way to prepare the sediment simulant. Mound studies have found the sediment simulant to be chemically comparable to contaminated sediments.[4]

The ACT*DE*CON^{SM} tests were run on a batch basis, using five contacts with a sediment to solution ratio of 1:20 by weight. Because of the high fines content of the sediment, a shaker was used for mixing to ensure adequate sediment contact with the ACT*DE*CON^{SM} chemicals. The tests were performed in duplicate in containers with resealable lids. Each batch contact consisted of mixing the sediment with the solution for 2 h. After centrifuging at 2,300 rpm for 5 min, the liquid fraction was decanted from the sediment. After the fifth wash, the sediment was rinsed with demineralized water and redried at 60°C for 24 h; then it underwent isotopic analysis for plutonium. The wash and rinse solutions were combined and also analyzed for plutonium.

I.1.2 Results of Optimization Testing

The results for the matrix of tests performed to establish the optimum ACT*DE*CON^{SM} formulation are presented in Table I.1. Test formulations 0 through 10 refer to the various proprietary chemical formulations tested. Decontamination factor (DF) is a ratio of the initial plutonium concentration (~500 pCi/g) divided by the residual concentration. The concentration on the sediment was normalized to its natural state, which accounts for the residual moisture (~25%) and the nonsilt material (~12%) removed prior to treatment. These quantities were estimated from the weight change of the processed sediment.

The test results obtained with various ACT*DE*CON^{SM} reagent concentrations demonstrated definite trends. Due to the proprietary nature of the formulations, actual concentrations are not reported. Variation of the concentration of the other reagents showed a trend towards an optimum concentration.

Test formulation 6 produced the highest plutonium removal. Normalizing the residual plutonium to the sediment's natural percent moisture and nonsilt material yielded a final concentration of plutonium in the spiked sediment after treatment with ACT*DE*CON^{SM} of 22 and 25 pCi/g for duplicate samples.

The results obtained with various ACT*DE*CON^{SM} reagent concentrations during the optimization studies demonstrated definite trends. Test formulations 0, 3, and 6 had the same concentration of chelant, and all three showed good DFs. Test formulation 9 contained a higher concentration of chelant; however, the DF obtained was not significantly greater to justify the increase in chelant concentration. The lowest concentration of chelant was used for tests 2, 5, and 8, and the DFs achieved for these three were significantly lower than for the other formulations. Variation of the concentration of the other reagents showed a trend towards an optimum concentration.

TABLE I.1 Results of Testing Various ACT*DE*CON^{SM} Formulations

Test Formulation[a]	Initial Plutonium Concentration (pCi/g)	Decontamination Factor[b]	Residual ^{238}Pu on Treated Sediment (pCi/g)	Normalized ^{238}Pu on Treated Sediment (pCi/g)
0	470	9.2, 7.0[c]	51, 68[c]	32, 43[c]
1	480	2.2	220	140
2	480	1.3	380	240
3	470	10.9	43	27
4	470	3.7	127	80
5	490	1.2, 3.1[c]	410, 160[c]	260, 100[c]
6	470	14, 12[c]	35, 40[c]	22, 25[c]
7	480	5.0	95	60
8	480	1.6, 3.1[c]	300, 150[c]	190, 95[c]
9	480	11	43	27.2
10	515	3.4, 4.7[c]	151, 110[c]	95, 70[c]

[a] Various proprietary chemical formulations.

[b] The decontamination factor is calculated by dividing the initial plutonium concentration in the sediment (dry weight) by the final plutonium concentration in the sediment (dry weight).

[c] Duplicate sample.

The results obtained with test formulation 6 demonstrated that the DF increased by 35% when compared with the standard ACT*DE*CON^{SM} formula (test formulation 0). In addition, the chemical content for test formulation 6 was reduced by 33%. On the basis of the observed trends and the desire to reduce the reagent concentrations to a minimum without reducing the DF, formulation 6 was chosen as the optimum.

I.1.3 Comparison of Batch Versus Percolation Tests

The optimum ACT*DE*CON^{SM} formula was used in a test designed to simulate the conditions that can arise in a proposed in-situ sediment washing technique. One possible approach to the full-scale application of this technique is the installation of a drainage system below the treatment zone. The wash solution, after mixing with the contaminated sediment, percolates down and is collected in the drainage system, where it is pumped out to be treated. To further evaluate the optimum formulation, a series of laboratory tests were performed to compare batch testing to percolation of the wash solution.

The important feature of the percolation test was the slow flow of the ACT*DE*CON^{SM} solution through the sediment. This type of application produces a much higher sediment to ACT*DE*CON^{SM} ratio within the sediment interstices than can occur in batch tests. The contact period is also far greater than during the batch tests.

Difficulties were experienced on such a small scale due to the fine fraction of the sediment being tested. The sediment was placed in a 0.5-in. diameter glass column having a sintered filter support and flow control valve. It was necessary to use a bed of washed laboratory fine sand to support the sediment and prevent fines in the sediment from blocking the sintered filter. In addition, a mixture of medium and fine sands were mixed with the sediment in a ratio of 4:1 to prevent "caking" and loss of flow.

The presence of sand within the sediment provided a mechanical aid to the ACT*DE*CON^{SM} flow, but it did not affect the chemistry of the process. The sand was required because the high silt/clay fraction of the sediment produces a densely packed impervious material that prevents drainage.

Other physical factors (such as channeling through the column) would tend to reduce the sediment/ACT*DE*CON^{SM} contact and hence the decontamination efficiency. However, at this scale it was not practical to agitate the sediment, as is intended at full scale. In spite of these difficulties, the DFs obtained were comparable to the batch equilibrium DFs (see Table I.2). It is expected that the mechanical difficulties described above will be resolved during pilot- and full-scale applications by use of a mechanical mixing device.

The plutonium concentrations on the treated sediment samples are presented in Table I.2. The results are reported for the optimum formulation in both the batch and percolation processes. Results from a triplicate test using the optimum formula show that sediment decontamination can be achieved using an in-situ approach.

I.1.4 Dissolution of Nonhazardous Minerals

A necessary part of the sediment remediation program is an evaluation of the impact of the ACT*DE*CON^{SM} process on such noncontaminant species as calcium, magnesium, potassium, aluminum, and iron. These species are present in the sediment in large concentrations. Consequently, any significant dissolution of these species by the ACT*DE*CON^{SM} process will have an impact on the ability of the treated sediment to support plant growth. Therefore, an assessment of the dissolution of these elements would give an indication of the impact the wash process will have on the structure and final quality of the sediment.

TABLE I.2 Decontamination Factors Obtained for Batch and Percolation Testing with the Optimum ACT*DE*CON^{SM} Formulation

Test	Decontamination Factor[a]	Residual ^{238}Pu on Treated Sediment (pCi/g)	Normalized ^{238}Pu on Treated Sediment (pCi/g)
Batch			
1	9.7	49	31
2	10	46	29
3	8	59	37
Percolation			
1	10	46	29
2	16	30	19
3	9.7	49	31

[a] The decontamination factor is calculated by dividing the initial plutonium concentration in the sediment (dry weight) by the final plutonium concentration in the sediment (dry weight).

The extent of the dissolution of mineral content was evaluated from triplicate tests in which Mound sediment was washed five times with the optimum formulation. The sediment was analyzed before and after contact. The difference in the concentration of the minerals was calculated, and the dissolved quantity per gram of mineral weight is presented in Table I.3. The total mineral weight is defined as the dried sediment weight minus the organic content weight.

The results presented in Table I.3 show that the combined dissolution of the calcium, magnesium, potassium, aluminum, and iron amounted to less than 3% of the total mineral content of the sediment. These data indicate that no inhibitor is required to minimize the dissolution of the sediment. During the actual field application, the dissolved mineral content is expected to stabilize if the ACT*DE*CON^{SM} solution is recycled.

TABLE I.3 Removal of Mineral Elements from the Sediment

Sample No.	Amount of Mineral Element Removed (mg/g)						Percent of Total Minerals Removed
	Ca	Mg	K	Al	Fe	Total	
1	18.8	nd[a]	nd	nd	2.1	20.9	2.3
2	17.5	nd	nd	nd	2.8	20.3	2.2
3	19.8	nd	nd	nd	2.1	21.9	2.4

[a] nd = not detected.

I.2 Ion-Exchange Studies (Tasks 4, 5, and 6)

I.2.1 Introduction

The spent ACT*DE*CON^{SM} solution resulting from treatment of sediments may be processed to remove the plutonium using the MAG*SEP^{SM} process. MAG*SEP^{SM} particles, coated with an appropriate adsorber material, can selectively remove plutonium. The choice of an adsorber material depends on the species present in the ACT*DE*CON^{SM} solution (i.e., the charge associated with the contaminant species) and the ultimate fate of the plutonium and/or the spent ACT*DE*CON^{SM} solution.

In order to identify a suitable adsorber, two different types of ion-exchange materials were examined with two different approaches in mind. The first approach was to examine the use of an inorganic cationic exchange material with the view to regenerate the chelant and, if required, provide a stable inorganic material for the final waste form. Using this approach, the acidic sites on the ion-exchange material break the plutonium-chelant complex and allow adsorption of cationic plutonium and the release of the chelant for reuse. The second approach examined the use of an anionic ion-exchange material to adsorb the anionic plutonium-containing species.

The testing described in this section of the report is a summary of the testing performed under the following tasks: Task 4 - Ion-Exchange Material Studies; Task 5 - Magnetic Particle Optimization Studies; and Task 6 - Magnetic Particle Regeneration Studies. This section also provides a history of the testing and the most recent results obtained with spent ACT*DE*CON^{SM} formulated to decontaminate Mound sediment.

I.2.2 Testing Using Cationic Materials

Experience within the nuclear industry has shown that inorganic ion exchangers, especially zeolites, demonstrate selectivity for certain radionuclides. A selection of inorganic exchangers was screened for ability to remove actinides from ACT*DE*CON^{SM} solutions, and the most promising candidates were tested for their selectivity toward plutonium.

The initial screening of candidate ion-exchange materials, performed concurrently with Tasks 1 and 2, used an ACT*DE*CON^{SM} formulation that was successful with the decontamination of other sediment types. The effect of interferences was examined with a spent simulant ACT*DE*CON^{SM} solution containing known concentrations of Ca and Fe. The concentrations of Ca and Fe in the simulant solution were chosen on the basis of analysis of samples resulting from previous testing on other sediment types. The simulant ACT*DE*CON^{SM} solution was spiked with ^{238}Pu as plutonium nitrate. The plutonium species in solution is believed to be the same as will form during process application.

Several cationic materials were tested: manganese dioxide, titanium dioxide, titanium phosphate, zirconium phosphate, transylvanian volcanic tuff (TVT) (a natural zeolite), and three silicon materials incorporating tin, manganese, and titanium, respectively.

Batch equilibrium tests were performed in ACT*DE*CON^{SM} solutions containing Ca (500 ppm); Mg (50 ppm); Fe (5 ppm); and Mn (5 ppm). The selectivity and capacity of the exchangers were compared. Two exchangers, zirconium phosphate and TVT, were chosen for column testing with plutonium-spiked ACT*DE*CON^{SM} solution.[5]

In the column tests, the exchangers were first brought to equilibrium with an ACT*DE*CON^{SM} solution containing uranium. The test solution was of the same composition but with an addition of 8.4 nCi/L ^{238}Pu as plutonium nitrate. The test solution passed through the column at a rate of 60 resin bed volumes per hour (b.v. hr^{-1}).[6] The TVT was the most satisfactory material under these conditions, removing more than 90% of the plutonium in one pass. The results are shown in Table I.4.

Once TVT was identified as the most promising material for plutonium removal, the next stage was to prepare MAG*SEP^{SM} particles containing TVT for testing with the simulant waste stream and optimizing the conditions of application (such as contact time and the ratio of particles to solution). In addition, a study of the conditions required to regenerate the particles was performed. MAG*SEP^{SM} particles were also prepared using the adsorber material amidoxime to compare the behavior of an organic adsorber with that of the inorganic adsorber.

After preparing MAG*SEP^{SM} particles of TVT and of amidoxime, tests with spent ACT*DE*CON^{SM} solution were conducted to optimize the application conditions. Since sediment from the Mound site was not available at this point of the program, the MAG*SEP^{SM} particles were exposed to a simulated ACT*DE*CON^{SM} solution containing 1,200 ppm calcium and 50 ppm iron. This solution was spiked with 3.2 nCi/L ^{238}Pu as plutonium nitrate. Duplicate batch equilibrium tests were conducted with both sets of particles. Contact time was varied from 5 min to 30 min. MAG*SEP^{SM} particle concentrations of 10 and 40 g/L of solution were tested. The results of these tests are

TABLE I.4 Adsorption of ^{238}Pu on the Zeolite TVT from an ACT*DE*CON^{SM} Solution Simulant

Percent of ^{238}Pu Adsorbed by TVT	Volume of Solution Treated (Bed-Volumes)
94.1	10
93.1	20
91.0	30
89.7	40
96.0	50
90.8	60
91.4	70
91.8	80
91.7	90
91.7	100

presented in Table I.5. In all cases the results show that ^{238}Pu was not adsorbed by the MAG*SEP^{SM} particles under these conditions.

These results raised two questions:

1. Was the effectiveness of the MAG*SEP^{SM} particles impaired by the higher concentration of calcium and/or iron?
2. Did the manufacturing process of preparing MAG*SEP^{SM} particles impair the effectiveness of the ion-exchange material?

In order to address these questions, an experiment was performed in which the adsorption properties of TVT powder and TVT MAG*SEP^{SM} particles were tested in the presence of Ca only and in the presence of Ca and Fe. These tests were performed as batch equilibrium tests with a simulant optimum ACT*DE*CON^{SM} solution spiked with plutonium. Contact time and particle concentration were not varied. The results of the experiments are presented in Table I.6.

These results showed between 97% and 99% removal of ^{238}Pu from solution in all conditions examined. At this time it was concluded that the preparation of MAG*SEP^{SM} particles did not alter the behavior of TVT. Since the spent ACT*DE*CON^{SM} solution resulting from sediment decontamination will contain iron, it was decided to continue the test program with TVT particles in the presence of iron and calcium.

TABLE I.5 MAG*SEP^{SM} Particle Optimization Study with TVT and Amidoxime Adsorbers

Sample Description	Contact Time (min)	Particle Concentration (g/L)	Sample A ^{238}Pu (pCi/mL)	Sample B ^{238}Pu (pCi/mL)
Untreated simulant	n/a[a]	n/a	3.2	3.2
TVT	5	10	3.4	3.2
TVT	10	10	2.6	3.0
TVT	30	10	3.2	3.2
TVT	5	40	3.4	3.2
Amidoxime	5	10	3.2	3.0
Amidoxime	10	10	3.2	3.2
Amidoxime	30	10	3.2	3.1
Amidoxime	5	40	3.4	3.2

[a] n/a = not applicable.

TABLE I.6 ^{238}Pu Adsorption Using Powdered TVT and TVT MAG*SEP^{SM} Particles

Adsorber Type	Particle Contact Time (min)	Particle Concentration (g/L)	Sample ^{238}Pu (pCi/mL)
*Simulant ACT*DE*CON^{SM} plus Ca*			
None	n/a[a]	n/a	21
Powdered TVT	30	25	0.14
TVT MAG*SEP^{SM}	30	25	0.21
*Simulant ACT*DE*CON^{SM} plus Ca and Fe*			
None	n/a	n/a	28
Powdered TVT	30	25	0.72
TVT MAG*SEP^{SM}	30	25	0.39

[a] n/a = not applicable.

The particle optimization studies were repeated using a simulant solution based on the optimum ACT*DE*CON^{SM} reagent concentrations. During these tests the TVT MAG*SEP^{SM} particles were also tested with two possible regenerating solutions: 3 M sodium nitrate and 3 M ammonium carbonate. The results of the optimization tests and regeneration studies are presented in Table I.7.

Table I.7 shows the results of testing a solution simulant with varying concentrations of TVT MAG*SEP^{SM} particles. The results show that at the highest particle concentration of 40 g/L, 17% of the ^{238}Pu was adsorbed by the particles. Regenerating those particles with 3 M ammonium carbonate yielded only 4% of the adsorbed plutonium.

During this period of testing, contaminated Mound site sediment was received in the Bradtec Ltd. laboratory. A portion of the sediment was washed with the optimum ACT*DE*CON^{SM} formulation. The ACT*DE*CON^{SM} solution from the first wash of the Mound sediment was treated immediately with two types of TVT MAG*SEP^{SM} particles. Duplicate 25-mL aliquots of the wash solution were contacted for 15 min with MAG*SEP^{SM} particles. The results of these tests are listed in Table I.8.

Although the concentration of ^{238}Pu in the spent ACT*DE*CON^{SM} wash solution was lower than in previous experiments with spiked plutonium, it was sufficient to conclude that the TVT MAG*SEP^{SM} particles were ineffective for ^{238}Pu removal.

TABLE I.7 Adsorption and Regeneration Studies Using TVT MAG*SEP^{SM} Particles

Sample Description	Contact Time (min)	TVT MAG*SEP^{SM} Particle Concentration (g/L)	Total ^{238}Pu Concentration (pCi)	$NaNO_3$ Regenerant ^{238}Pu (pCi)	$(NH_4)_2CO_3$ Regenerant ^{238}Pu (pCi)
Untreated Sample A	n/a[a]	n/a	529	n/a	n/a
Untreated Sample B	n/a	n/a	551	n/a	n/a
Sample A	5	10	518	< 0.8	-
Sample B	5	10	554	-	5.4
Sample A	10	10	599	2.4	-
Sample B	10	10	462	-	4.3
Sample A	30	10	513	4.9	-
Sample B	30	10	513	-	3.8
Sample A	5	40	416	3.8	-
Sample B	5	40	486	-	21.6

[a] n/a = not applicable.

Discussions with the supplier of the TVT adsorber indicated that the inconsistent behavior of TVT may be due to the activation method of the material. In all previous tests, the TVT had been thermally activated. The TVT supplier suggested activating the material with acid.

A series of batch equilibrium tests were performed with TVT powder that was reactivated using heat and/or acid. Duplicate samples of TVT powder were exposed for 15 min each to the optimum ACT*DE*CON^{SM} solution containing iron and calcium and spiked with ^{238}Pu. The results are shown in Table I.9. No adsorption of ^{238}Pu was detectable in these tests,which suggested that the activation method for TVT powder was not a factor in the inconsistent behavior of this adsorber.

At this point in the program it was decided to reexamine other inorganic cationic ion-exchange materials to determine if the inconsistent behavior exhibited by TVT was specific to TVT or was exhibited by other materials. Manganese dioxide powder, zirconium phosphate powder, thermally activated TVT powder, and acid-activated TVT powder were tested with the optimum

TABLE I.8 Treatment of Spent ACT*DE*CON^{SM} from Contaminated Mound Sediment with TVT MAG*SEP^{SM} Particles

Sample Description	Contact Time (min)	TVT MAG*SEP^{SM} Particles Concentration (g/L)	Total ^{238}Pu Concentration (pCi)
Untreated spent ACT*DE*CON^{SM} solution after one wash - Sample A	n/a[a]	n/a	58.3
Untreated spent ACT*DE*CON^{SM} solution after one wash - Sample B	n/a	n/a	76.7
Spent ACT*DE*CON^{SM} solution treated with Type 1 TVT MAG*SEP^{SM} particles - Sample A	15	20	59.7
Spent ACT*DE*CON^{SM} solution treated with Type 1 TVT MAG*SEP^{SM} particles - Sample B	15	20	62.4
Spent ACT*DE*CON^{SM} solution treated with Type 2 TVT MAG*SEP^{SM} particles - Sample A	15	20	77.5
Spent ACT*DE*CON^{SM} solution treated with Type 2 TVT MAG*SEP^{SM} particles - Sample B	15	20	68.0

[a] n/a = not applicable.

ACT*DE*CON^{SM} solution artificially spiked with ^{238}Pu. The tests were performed in the presence and absence of Fe and/or Ca. For each test, 0.5 g of the ion-exchange material was contacted with 25 mL of simulant for 15 min. The results of these experiments are presented in Table I.10.

Approximately 78% of the ^{238}Pu was removed with zirconium phosphate when iron was not present in the test solution. Manganese dioxide adsorbed less than 5% of the plutonium, probably because of insufficient contact time.[7] The acid-activated and thermally activated TVT behaved the same as in the previous tests, with neither material adsorbing a measurable quantity of plutonium. Since iron would be present in spent ACT*DE*CON^{SM} solution, it was concluded that neither zirconium phosphate nor manganese dioxide were suitable alternatives to TVT powder.

TABLE I.9 Treatment of Simulant Spent ACT*DE*CON^{SM} Solution Using TVT Powder Activated by Heat and/or Acid Rinse

Sample Description	Contact Time (min)	TVT MAG*SEP^{SM} Particles Concentration (g/L)	Total ^{238}Pu Concentration (pCi)
Untreated simulant ACT*DE*CON^{SM} - Sample A	n/a[a]	n/a	132
Untreated simulant ACT*DE*CON^{SM} - Sample B	n/a	n/a	130
Spent ACT*DE*CON^{SM} solution treated with thermally-activated TVT powder - Sample A	15	20	132
Spent ACT*DE*CON^{SM} solution treated with thermally-activated TVT powder - Sample B	15	20	132
Spent ACT*DE*CON^{SM} solution treated with acid-activated TVT powder - Sample A	15	20	127
Spent ACT*DE*CON^{SM} solution treated with acid-activated TVT powder - Sample B	15	20	127
Spent ACT*DE*CON^{SM} solution treated with thermally- and acid-activated TVT powder - Sample A	15	20	130
Spent ACT*DE*CON^{SM} solution treated with thermally- and acid-activated TVT powder - Sample B	15	20	130

[a] n/a = not applicable.

By this point in the program of work, the ACT*DE*CON^{SM} formulation had been modified for decontamination of weathered contaminated Mound sediment. Therefore, one final verification test was performed with the TVT material. A new batch of TVT was obtained from the supplier and activated. Samples of the new batch and the existing batch of TVT were preconditioned with carbonate, and batch equilibrium experiments were performed. Duplicate samples (20 g/L) of the new TVT adsorber and the existing TVT adsorber were each exposed for 15 min to the modified ACT*DE*CON^{SM} formulation simulant and the optimum ACT*DE*CON^{SM} formulation simulant. Both solutions had been spiked with plutonium to enhance the analysis. The optimum ACT*DE*CON^{SM} solution was fortified with calcium, as in the previous tests. The results of these tests are presented in Table I.11.

TABLE I.10 Removal of ^{238}Pu with Zirconium Phosphate, Manganese Dioxide, and TVT in the Presence and Absence of Calcium and/or Iron

Ion-Exchange Material	^{238}Pu in Simulant without Ca and Fe (pCi/mL)	^{238}Pu in Simulant with Ca (pCi/mL)	^{238}Pu in Simulant with Fe (pCi/mL)	^{238}Pu in Simulant with Ca and Fe (pCi/mL)
Untreated simulant ACT*DE*CON^{SM} solution	49	-	-	-
Untreated simulant ACT*DE*CON^{SM} solution	-	62.1	-	-
Untreated simulant ACT*DE*CON^{SM} solution	-	-	64.8	-
Untreated simulant ACT*DE*CON^{SM} solution	-	-	-	64.8
Zirconium phosphate	10.8	-	-	-
Zirconium phosphate	-	13.5	-	-
Zirconium phosphate	-	-	62.1	-
Zirconium phosphate	-	-	-	59.4
Manganese dioxide	45.9	-	-	-
Manganese dioxide	-	56.7	-	-
Manganese dioxide	-	-	59.4	-
Manganese dioxide	-	-	-	59.4
Thermally-activated TVT powder	48.6	-	-	-
Thermally-activated TVT powder	-	62.1	-	-
Thermally-activated TVT powder	-	-	64.8	-
Thermally-activated TVT powder	-	-	-	62.1
Acid-activated TVT powder	48.6	-	-	-
Acid-activated TVT powder	-	62.1	-	-
Acid-activated TVT powder	-	-	62.1	-
Acid-activated TVT powder	-	-	-	62.1

TABLE I.11 TVT Treatment of the Modified ACT*DE*CON^{SM} Formulation and the Optimum ACT*DE*CON^{SM} Formulation Simulants

Sample Description	Total ^{238}Pu Concentration (pCi)
Untreated ACT*DE*CON^{SM} solution	135
Untreated optimum ACT*DE*CON^{SM} solution containing calcium	192
ACT*DE*CON^{SM} solution treated with TVT MAG*SEP^{SM} particles - Sample A	135
ACT*DE*CON^{SM} solution treated with TVT MAG*SEP^{SM} particles - Sample B	135
ACT*DE*CON^{SM} solution treated with TVT powder - Sample A	135
ACT*DE*CON^{SM} solution treated with TVT powder - Sample B	135
ACT*DE*CON^{SM} solution treated with granular TVT (New batch) - Sample A	135
ACT*DE*CON^{SM} solution treated with granular TVT (New batch) - Sample B	138
Optimum ACT*DE*CON^{SM} solution treated with granular TVT (New batch) - Sample A	189
Optimum ACT*DE*CON^{SM} solution treated with granular TVT (New batch) - Sample B	192

Again it was observed that the TVT adsorber did not remove plutonium from either ACT*DE*CON^{SM} solution. Testing on cation-exchange materials was, therefore, suspended. It was decided to evaluate the form of the plutonium species present in the spent ACT*DE*CON^{SM} solution following treatment of Mound sediment.

I.2.3 Testing Using Anionic Materials

During early testing[8] a spent ACT*DE*CON^{SM} solution resulting from the treatment of artificially contaminated Mound sediment was passed through an anion-exchange column (Amberlite IRA-420). Under these conditions, approximately 89% of the ^{238}Pu was removed from the spent ACT*DE*CON^{SM} solution. Testing using anion-exchange resins had been suspended to concentrate on cation-exchange materials, because it was hypothesized that the chelant in the ACT*DE*CON^{SM} solution could be regenerated by the cationic adsorbers. However, as the program of work progressed and problems were experienced with the cation-exchange materials, testing with anion-exchange materials was resumed.

Batch equilibrium tests were performed with anion-exchange-resin-coated MAG*SEP^{SM} particles and pure anion-exchange resin. The following four solutions were contacted with the anion-exchange materials.

Solution 1	Modified ACT*DE*CON^{SM} solution resulting from treatment of Mound sediment. This solution was also spiked with ^{238}Pu as plutonium nitrate to allow analysis using gross alpha spectroscopy.

Solution 2	Modified ACT*DE*CON^{SM} solution simulant spiked with ^{238}Pu as plutonium nitrate.
Solution 3	Modified ACT*DE*CON^{SM} solution simulant spiked with 0.001 M iron and ^{238}Pu as plutonium nitrate.
Solution 4	Modified ACT*DE*CON^{SM} solution simulant spiked with 0.03 M calcium and ^{238}Pu as plutonium nitrate.

Table I.12 presents the results of this matrix of tests. No significant adsorption of ^{238}Pu was observed. These experiments differed from previous tests with anion resin in that they were performed as batch equilibrium tests instead of column tests. Also, the previous successful tests had an anion concentration that was approximately one-tenth of the concentration of these tests.

In order to determine if the low ^{238}Pu adsorption was due to the test being a batch equilibrium test, a column test with the spent modified ACT*DE*CON^{SM} solution (Solution 1) was performed. In this test, anion ion-exchange resin was loaded in a column and preconditioned with carbonate solution. The results of this test are provided in Table I.13.

The results show that it is possible to adsorb ^{238}Pu on an anion-exchange resin using an ion-exchange column. This result confirmed that some of the ^{238}Pu was present in an anionic form in the modified ACT*DE*CON^{SM} solution. More than 31% of the plutonium was adsorbed on the anion resin. This amount corresponds to the capacity of the resin that was used in the column experiment. Therefore, incomplete adsorption may have been caused by insufficient capacity on the ion-exchange resin or the carbonate concentration in the solution not being high enough to be an effective regenerant of the resin, causing the ^{238}Pu to be desorbed as rapidly as it was being adsorbed.

In order to resolve this issue, a test was performed in which the modified ACT*DE*CON^{SM} solution was diluted by a factor of ten prior to adsorption on an anion ion-exchange column. The column was subsequently washed with 1.0 M sodium carbonate to determine if the ^{238}Pu that was loaded on the resin could be regenerated. This test showed that the quantity of anion-exchange resin used was sufficient to retain all the anions.

Another important issue of the ion-exchange studies was whether the plutonium was present as the anionic plutonium-chelant complex, a carbonate complex, or in another form that was preventing the plutonium from being adsorbed (i.e., a neutral or cationic colloid or humic/fulvic acid complex).

An examination of the speciation of the plutonium in the contaminated Mound sediment (see Section I.3) showed that between 52% and 55% of the plutonium was associated with the

TABLE I.12 Treatment of ACT*DE*CON^{SM} Solutions with an Anion-Exchange Material

Sample Description	Contact Time (min)	Particle Concentration (g/L)	^{238}Pu Concentration (pCi/mL)
Solution 1 - Untreated	n/a	n/a	138
Solution 1 - Treated with MAG*SEP^{SM} particles (Sample A)	15	20	138
Solution 1 - Treated with MAG*SEP^{SM} particles (Sample B)	15	20	143
Solution 1 - Treated with MAG*SEP^{SM} particles (Sample A)	2	20	135
Solution 1 - Treated with MAG*SEP^{SM} particles (Sample B)	2	20	146
Solution 1 - Treated with MAG*SEP^{SM} particles (Sample A)	15	4	130
Solution 1 - Treated with MAG*SEP^{SM} particles (Sample B)	15	4	130
Solution 1 - Treated with MAG*SEP^{SM} particles (Sample A)	2	4	148
Solution 1 - Treated with MAG*SEP^{SM} particles (Sample B)	2	4	135
Solution 2 - Untreated	n/a	n/a	140
Solution 2 - Treated with MAG*SEP^{SM} particles (Sample A)	15	20	132
Solution 2 - Treated with MAG*SEP^{SM} particles (Sample B)	15	20	130
Solution 3 - Untreated	n/a	n/a	154
Solution 3 - Treated with MAG*SEP^{SM} particles (Sample A)	15	20	132
Solution 3 - Treated with MAG*SEP^{SM} particles (Sample B)	15	20	130
Solution 4 - Untreated	n/a	n/a	116
Solution 4 - Treated with MAG*SEP^{SM} particles (Sample A)	15	20	132
Solution 4 - Treated with MAG*SEP^{SM} particles (Sample B)	15	20	138
Solution 4 - Treated with resin (Sample A)	15	20	132
Solution 4 - Treated with resin (Sample B)	15	20	127

TABLE I.13 ^{238}Pu Adsorption on an Anion Ion-Exchange Resin

Sample Description	^{238}Pu Concentration (pCi/mL)
Solution 1 - Untreated	138
Solution 1 - Treated using an anion exchange column	43.2

organic matter in the sediment. Post-wash speciation of the sediment showed that the plutonium associated with the organic fraction was reduced by 97%. Hence, it is possible that a significant quantity of the plutonium is bound with these organic acids.

The results of the speciation study also showed that approximately 43% of the plutonium was present as or associated with the oxide fraction of the sediment. Approximately 88% of this fraction of the plutonium was extracted with the wash solution. Therefore, it is possible that a significant portion of the plutonium was adsorbed onto inorganic colloidal material. This result suggests that the plutonium present in the spent ACT*DE*CON^{SM} solution is not totally in the form originally postulated (i.e., a plutonium-chelant or carbonate complex). Neutral or cationic species would not be adsorbed by an anionic resin.

The issue was resolved by ensuring that the plutonium complex formed in the simulant spent ACT*DE*CON^{SM} solution was the intended anionic plutonium-chelant or carbonate complex. The plutonium-chelant complex was first formed by the addition of plutonium nitrate to the chelant in an acidic environment (i.e., the pH of the chelant solution in the hydrogen form). Carbonate was added to the solution until the required carbonate concentration was obtained. Using this method of preparation, the anionic $Pu[chelant]^{2-}$ and plutonium carbonate species are formed in preference to any other species and, consequently, should adsorb on an anion exchange column. If the species formed during decontamination of the contaminated Mound sediment is not the expected $Pu[chelant]^{2-}$ or carbonate complex but another species that is cationic or neutral, then the inability of the anion-exchange resin and MAG*SEP^{SM} particles to adsorb the plutonium complexes is explained.

Tests were performed at two different pH values, 9.0 and 11.0, and two different carbonate concentrations, 0.1 M and 1.0 M, to determine if, at a higher pH, the ^{238}Pu species is "more anionic" and hence retained more efficiently. Regeneration of the anionic ion-exchange columns with 1.0 M sodium carbonate was also performed at these two pH values. The results are presented in Tables I.14 and I.15.

The results of these tests led to the following conclusions:

1. In the absence of other complexing species or colloidal species that may be present in sediment, anionic plutonium-chelant or carbonate species were formed.
2. The anionic plutonium complex was adsorbed by the anion-exchange resin in the stronger carbonate concentration of the modified ACT*DE*CON^{SM} formulation.
3. The percentage adsorption of the anionic plutonium complex was reduced 10% when the pH was lowered from 11.0 to 9.0.

TABLE I.14 Removal of ^{238}Pu Using an Anion Exchange Column

Column Number	Sample Description	^{238}Pu in Column Influent (pCi)	^{238}Pu in Column Effluent (pCi)	^{238}Pu Retained on Column[a] (pCi)	Total ^{238}Pu Removal (%)
A	0.1 M CO_3^{2-} at pH 9.0	3,112	< 135	>2,977	>96
B	0.1 M CO_3^{2-} at pH 11.0	2,889	< 135	>2,754	>95
C	1.0 M CO_3^{2-} at pH 9.0	3,119	751	2,368	76
D	1.0 M CO_3^{2-} at pH 11.0	3,065	417	2,646	86

[a] ^{238}Pu retained is the difference between ^{238}Pu in the column influent and in the column effluent.

4. 1.0 M carbonate was an effective regenerant for the anionic plutonium species formed in the simulant solutions.

Following successful completion of these tests, the same test was performed with the modified ACT*DE*CON^{SM} solution resulting from treatment of contaminated Mound sediment. This solution was not spiked with additional plutonium prior to column testing to avoid the possibility of obtaining misleading results due to a difference in behavior between plutonium extracted from the sediment and plutonium added as a nitrate spike. A test was also performed in which the modified ACT*DE*CON^{SM} solution was diluted by a factor of ten prior to loading on the anion-exchange resin to determine if a reduction in carbonate concentration affected the percentage of plutonium adsorbed.

These latter tests were performed in the same manner as previous tests. The modified ACT*DE*CON^{SM} solution and the diluted spent solution were loaded onto the columns at a flow rate of approximately 1 mL/min. The concentration of ^{238}Pu in the modified ACT*DE*CON^{SM} solution resulting from decontamination of the contaminated Mound sediment was approximately 5.94 pCi/mL. The columns were washed with two bed volumes of deionized water, and the water washes were combined with the column effluent. The columns were then washed with 1.0 M sodium carbonate to determine the regeneration efficiency of the adsorbed plutonium. The spent regenerant was also submitted for analysis. The results of these tests with the modified ACT*DE*CON^{SM} solution are presented in Tables I.16 and I.17.

TABLE I.15 Percent of ^{238}Pu Regenerated with a 1.0 M Carbonate Solution

Column Number	Regenerant	^{238}Pu in Column Regenerant (pCi)	Percent ^{238}Pu Regenerated[a]
A	1.0 M CO_3^{2-} at pH 9.0	2,700	87
B	1.0 M CO_3^{2-} at pH 11.0	2,403	83
C	1.0 M CO_3^{2-} at pH 9.0	2,041	86
D	1.0 M CO_3^{2-} at pH 11.0	2,243	85

[a] The percent ^{238}Pu regenerated is obtained by dividing the ^{238}Pu found in the column regenerant by the ^{238}Pu retained on the column (Table I.14) and multiplying by 100.

TABLE I.16 Removal of ^{238}Pu from ACT*DE*CON^{SM} Solution with an Anion-Exchange Column

Column Number	Sample Description	^{238}Pu in Column Influent (pCi)	^{238}Pu in Column Effluent (pCi)	^{238}Pu Retained[a] on Column (pCi)	Total ^{238}Pu Removal (%)
A	Spent ACT*DE*CON^{SM} Solution	149	21.3	127	86
B	Dilute Spent ACT*DE*CON^{SM} Solution	149	0.2	148	100

[a] ^{238}Pu retained is the difference between ^{238}Pu in the column influent and in the column effluent.

TABLE I.17 Percent of ^{238}Pu Regenerated with 1.0 M Sodium Carbonate

Column Number	Regenerant	^{238}Pu in Column Regenerant (pCi)	Percent ^{238}Pu Regenerated[a] (%)
A	1.0 M CO_3^{2-} at pH 9.0	36.7	29
B	1.0 M CO_3^{2-} at pH 9.0	21.7	15

[a] The percent ^{238}Pu regenerated was obtained by dividing the ^{238}Pu found in the column regenerant by the ^{238}Pu retained on the column (Table I.16) and multiplying by 100.

It was noted during these tests that the dark brown coloration in the modified ACT*DE*CON^{SM} solution (presumably due to dissolved fulvic and humic acids) was retained by the anion resin and that the effluent from the column was completely clear. The coloration was not removed during the washing step with 1.0 M sodium carbonate. From this test it was possible to conclude that the loading characteristics of the modified ACT*DE*CON^{SM} solution were the same as those for the modified ACT*DE*CON^{SM} solution simulant. The ^{238}Pu retention was approximately 86% with the modified ACT*DE*CON^{SM} solution, whereas 100% adsorption of ^{238}Pu was observed with the simulant solution. The differences between the two solutions became apparent during the regeneration step. Approximately 86% of the ^{238}Pu was eluted from the column loaded with the simulant using 1.0 M sodium carbonate, but the percentage eluted was reduced to approximately 29% when the column was loaded with the modified ACT*DE*CON^{SM} solution.

This behavior suggested that the ^{238}Pu species in the modified ACT*DE*CON^{SM} solution was not entirely as expected (i.e., Pu-chelant or carbonate complex). It was possible that the plutonium was associated with a species strongly adsorbed on the column, such as an organic acid or inorganic anion.

I.2.4 Other Tests

Other tests were performed at the same time as the studies of the various ion-exchange materials for MAG*SEP^{SM} in order to gain more information regarding the chemical nature of the

^{238}Pu species after treatment with ACT*DE*CON^{SM}. These tests are described in this section of the report.

I.2.4.1 Ultrafiltration Studies

Two tests were performed to determine if significant plutonium adhered to colloidal matter present in the ACT*DE*CON^{SM} solution and to determine if the behavior of the plutonium differed when the test solutions were artificially spiked with ^{238}Pu. The tests used spent modified ACT*DE*CON^{SM} solution resulting from treatment of contaminated Mound sediment.

An aliquot from the combined modified ACT*DE*CON^{SM} solution and water washes resulting from treatment of triplicate samples of active Mound sediment was removed for the purpose of these tests. A fraction of the aliquot was artificially spiked with 27 pCi/mL ^{238}Pu, as plutonium nitrate, and allowed to stand for a few days prior to filtration through a 0.2-µm glass-fiber filter. This test was performed to assess whether sediment colloids that formed in the solution with time adsorb ^{238}Pu.

A second fraction of the aliquot was filtered through a 0.2-µm glass-fiber filter. The filtrate was then divided into two. Half of the solution was artificially spiked with 27 pCi/mL ^{238}Pu to enhance the concentration sufficiently to permit analysis by gross alpha spectroscopy. This test was performed to identify if the plutonium from the spiked sample behaves differently from the plutonium washed from the sediment. Both ACT*DE*CON^{SM} solutions (spiked and nonspiked) were passed through an ultrafiltration system consisting of the following filter sizes: 100,000 MW (molecular weight), 30,000 MW, and 3,000 MW. (The 100,000-MW filter will retain small sediment colloids, the 30,000-MW filter will retain humic acid colloids and larger fulvic acid colloids, and the 3,000-MW filter will retain the smaller humic and fulvic acid colloids. True chelant complexes and fulvic acid complexes as well as very small colloids will appear in the fraction passing through a 3,000-MW filter.) An aliquot of the solution passing through each filter was removed and analyzed for ^{238}Pu. (^{238}Pu in the nonspiked ACT*DE*CON^{SM} solution was analyzed by isotopic analysis since the ^{238}Pu concentration was insufficient for gross alpha determination to be reliable.) The results of the experiments are presented in Table I.18.

No difference in ^{238}Pu concentration was observed between modified ACT*DE*CON^{SM} solution spiked with ^{238}Pu that had been allowed to stand for two days before being filtered through a 0.2-µm filter and modified ACT*DE*CON^{SM} solution that had been prefiltered before being spiked with ^{238}Pu.

TABLE I.18 Ultrafiltration Results with ACT*DE*CON^{SM} Solutions

	Total ^{238}Pu Concentration	
Filter Size	Nonspiked ACT*DE*CON^{SM} (pCi/mL)	Spiked ACT*DE*CON^{SM} (pCi/mL)
Unfiltered	5.9	35.1
0.2 micron	5.9	29.7
100,000 MW	5.9	35.1
30,000 MW	4.2[a]	35.1
3,000 MW	4.9[a,b]	29.7

[a] The results obtained after passing the solution through a 30,000 MW and 3,000 MW filter can be considered equal, within experimental error.

[b] Most of the color was lost from the ACT*DE*CON^{SM} solution after passing through a 3,000 MW filter.

From these tests, it was possible to conclude the following:

1. 76% of the ^{238}Pu was present either in true solution or as colloids with size < 3,000 MW. Hence, most of the ^{238}Pu was not associated with larger sediment colloids or larger humic acid complexes.

2. ^{238}Pu was unlikely to be associated with humic acid, because most of the brown coloration of the ACT*DE*CON^{SM} solution was removed on passing through a 3,000-MW filter, but the ^{238}Pu was not removed. The strong coloration in the ACT*DE*CON^{SM} solution is primarily caused by dissolved humic acids.

3. 23.6% of the ^{238}Pu is removed by the 30,000-MW filter and, hence, is present in a form different from that expected with the chelant complex (where the molecular weight would be on the order of 500).

I.2.4.2 Plutonium Speciation in ACT*DE*CON^{SM} Sediment Solutions

The results of the ion-exchange tests to this point in the program of work had demonstrated that it was possible to remove 86% of the ^{238}Pu present in the spent ACT*DE*CON^{SM} solution using a strong anion-exchange resin (IRA 420). However, the resin was not selective for plutonium, and its present form was not practical for use in a process step. It was necessary, therefore, to put more emphasis on the identification of the plutonium species present in the modified ACT*DE*CON^{SM} solution so that the MAG*SEP^{SM} process can be made selective or an alternative method for treating the waste stream can be proposed.

In order to provide more information concerning the ^{238}Pu species present in the modified ACT*DE*CON^{SM} solution, the following program of work was performed. The overall objective of this investigation was to determine whether plutonium was associated with fulvic/humic acids or chelant/carbonate complexes in spent ACT*DE*CON^{SM} solutions resulting from the decontamination of contaminated Mound sediment. Speciation modeling, using the HAPHREEQ code, showed that the predominant plutonium species in these solutions should be $Pu(CO_3)_4^{4-}$, although complexes such as $PuO_2(CO_3)_3^{5-}$ have been reported in aqueous solutions at pH 8/9.[9] To determine whether plutonium was complexed with fulvic/humic acids in a modified ACT*DE*CON^{SM} solution resulting from the decontamination of contaminated Mound sediment, the solution must be separated into fractions containing fulvic/humic acids and chelant/carbonate complexes, and the plutonium concentration in each fraction must be determined. If it can be shown that there is a direct correlation between plutonium concentration and total organic concentration (TOC) in the fractions, this provides direct evidence of association of plutonium with fulvic/humic acids or chelant, depending on which fraction shows the correlation.

The ACT*DE*CON^{SM} solution used was obtained from a single contact with weathered Mound sediment and, therefore, contained the highest concentration of ^{238}Pu, organic matter, and other species extracted by the reagent. Thus, the testing was performed on a solution in which any interaction of organic or other species with ^{238}Pu was not diluted by subsequent washes. Twenty milliliters of DEAE cellulose was placed in a column and washed with deionized water. Aliquots of the ACT*DE*CON^{SM} solution (2, 5, and 10 mL) were loaded onto the column and washed through the column with deionized water.

It was observed that as a result of the deionized water elution, a brown band separated from the main brown band that had adhered to the top of the column. It was possible to collect the separated band using deionized water. Examination of this band using fluorescence spectroscopy showed no fluorescence (therefore, the sample was unlikely to be fulvic/humic acid). The band was retained for analysis of TOC, ^{238}Pu, and Fe.

Washing the column with water was continued until examination of the eluent by UV spectroscopy showed that the elution of chelant was complete. The second, and seemingly larger, brown band remained adhered to the column throughout the water washing. This band could not be removed using 0.5 M sodium hydroxide and was eventually removed as efficiently as possible by soaking the band in 2 M sodium hydroxide. This solution was retained for analysis of TOC, ^{238}Pu, and Fe. The results from the analysis are shown in Tables I.19 and I.20 for the water elution and the remaining band, respectively.

TABLE I.19 Analysis of TOC, Iron, and ^{238}Pu in the Water Fraction

Sample Description	TOC (ppm)	Iron (ppm)	^{238}Pu (pCi/mL)
10 mL ACT*DE*CON^{SM}	3,300	18	20
10 mL ACT*DE*CON^{SM}	6,600	120	35.1
10 mL ACT*DE*CON^{SM}	2,100	35	6.5
10 mL ACT*DE*CON^{SM}	5,800	76	26.5
5 mL ACT*DE*CON^{SM}	5,000	47	26.2
2 mL ACT*DE*CON^{SM}	2,200	16	8.9
2 mL ACT*DE*CON^{SM}	1,000	2.2	6.2

TABLE I.20 Analysis of TOC, Iron, and ^{238}Pu in the 2 M Sodium Hydroxide Extracted Fraction

Sample Description	TOC (ppm)	Iron (ppm)	^{238}Pu (pCi/mL)
10 mL ACT*DE*CON^{SM}	910	1.7	2.9
10 mL ACT*DE*CON^{SM}	1,200	10	1.6
5 mL ACT*DE*CON^{SM}	2,800	1.6	9.5
2 mL ACT*DE*CON^{SM}	360	4.4	8.6
2 mL ACT*DE*CON^{SM}	910	1.3	0.3

The concentrations of TOC, Fe, and ^{238}Pu for the water fractions and the sodium hydroxide fractions were plotted against one another. No correlation was observed between any of the species in the sodium hydroxide fraction. However, a correlation was observed between each species with each of the other two species in the brown band eluted with the water wash. These correlations are represented graphically in Figures I.2-I.4.

It was interesting to note that a correlation exists not only between TOC and ^{238}Pu and between TOC and Fe but also between ^{238}Pu and Fe. The color of an Fe-chelant complex was the same as the color of the band eluted with water. Therefore, it is reasonable to assume that this band contained the Fe-chelant complex, as opposed to a humic/fulvic species, which would have shown fluorescence. As the ^{238}Pu was exhibiting similar chemical behavior to the iron (i.e., ^{238}Pu correlates with TOC and was concentrated in the band), it is reasonable to assume that the ^{238}Pu in this fraction was also present as a chelant complex. This fraction contained in excess of 70% of the total ^{238}Pu activity.

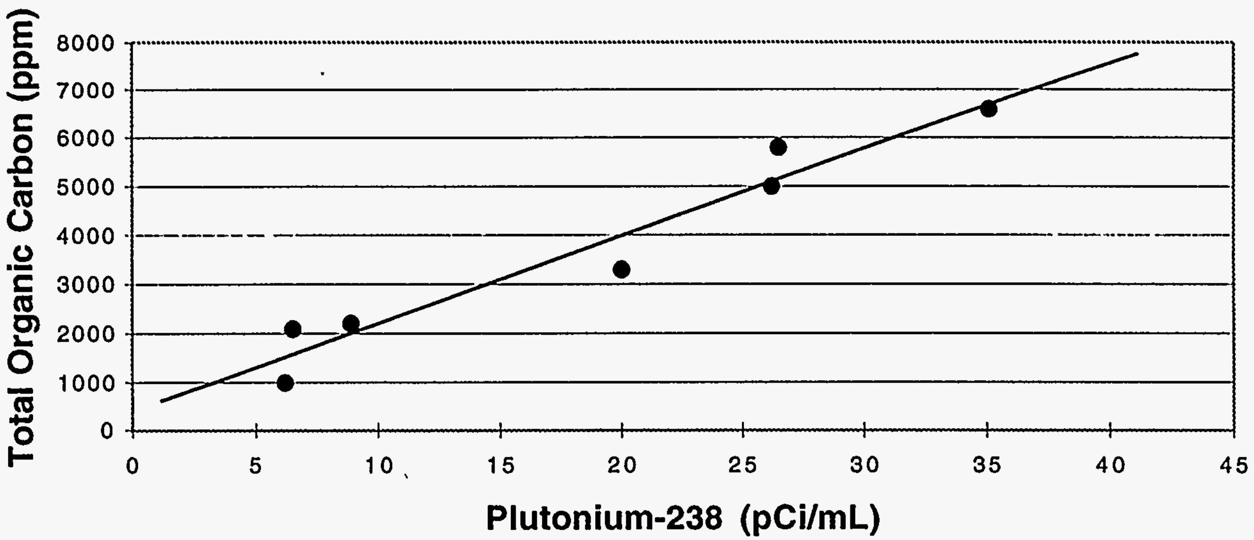

FIGURE I.2 Correlation between TOC and Plutonium Concentrations in the Water Fractions

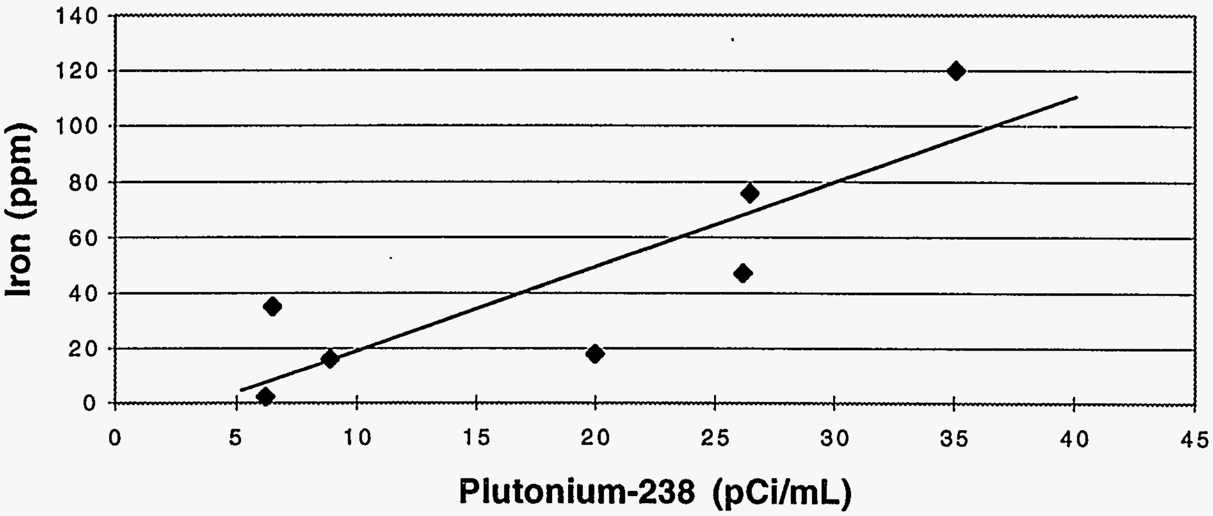

FIGURE I.3 Correlation between Iron and Plutonium Concentrations in the Water Fractions

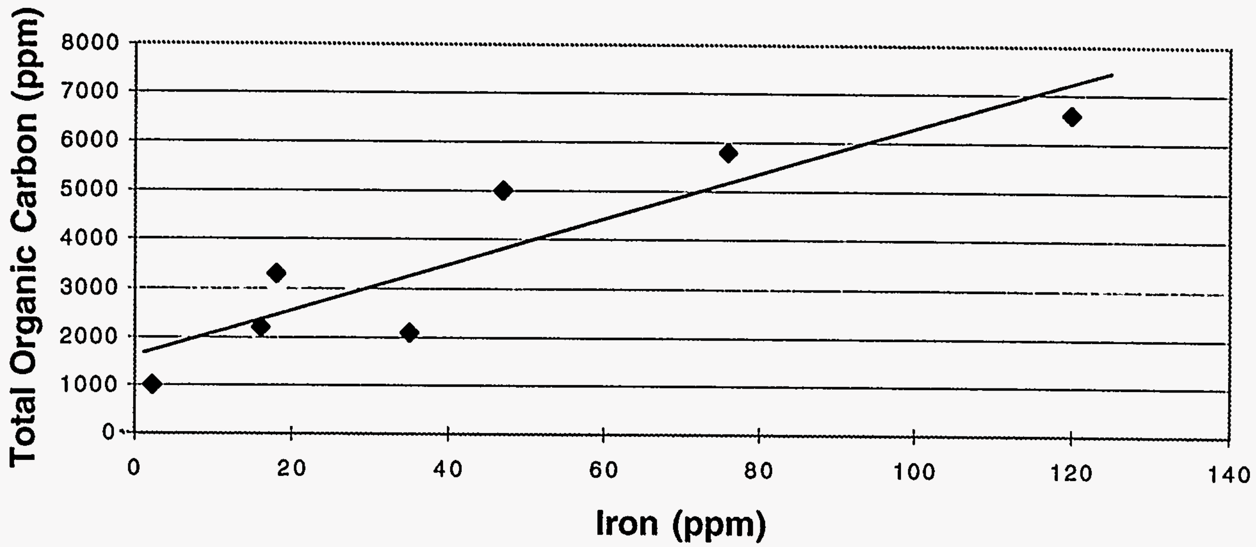

FIGURE I.4 Correlation between TOC and Iron Concentrations in the Water Fractions

I.2.4.3 Plutonium Adsorption on Strong Anion Resin from a Fresh Solution of Modified ACT*DE*CON^{SM}

From the results of the previous test (Section I.2.4.2), it appeared that the majority of the plutonium was associated with the chelant in the spent modified ACT*DE*CON^{SM} solution. Accordingly, the majority of the ^{238}Pu should be eluted from a strong anion-exchange resin and behave in the same manner as was observed in the test reported in Section I.2.3, Tables I.14 and I.15. To test this theory, the same solution that was used for the testing using DEAE cellulose was used to test the behavior of ^{238}Pu on Amberlite IRA-420. The tests were performed as described below.

Forty milliliters of Amberlite IRA 420 strong anion resin were placed in a column, preconditioned with carbonate, and washed with deionized water until the washes were neutral. A 25-mL solution of modified ACT*DE*CON^{SM} (approx. 10 days old) was diluted to 250 mL with deionized water and loaded onto the column at a rate of 1 mL/min. After loading, the column was washed with two bed volumes of water, which were combined with the loading effluent. The sample was retained and analyzed for ^{238}Pu. An analogous test was also done using undiluted solution of modified ACT*DE*CON^{SM} for comparison. After the ACT*DE*CON^{SM} solution was loaded, the column was regenerated with five bed volumes of 1.0 M sodium carbonate and then washed with water. It was noted at this point that a brown band at the top of the column was not eluted with carbonate, and attempts to remove this band with methanol, acetonitrile, and 8 M nitric acid were unsuccessful. The 1.0 M sodium carbonate regenerant was analyzed for ^{238}Pu. The results from this testing are presented in Tables I.21 and I.22.

The results show that the behavior of the ^{238}Pu in the modified ACT*DE*CON^{SM} was as expected if the ^{238}Pu was associated with the chelant. The reasons why the results are different from a similar test reported in Section I.2.2, Tables I.16 and I.17, are unknown, but the different results may be due to an aging effect occurring in the spent ACT*DE*CON^{SM} solution. This earlier test was performed on a solution that was approximately one month old.

TABLE I.21 Removal of ^{238}Pu from ACT*DE*CON^{SM} Solution Using an Anion-Exchange Column

Column Number	Sample Description	^{238}Pu in Column Influent (pCi)	^{238}Pu in Column Effluent (pCi)	^{238}Pu Retained[a] on Column (pCi)	Total ^{238}Pu Removed (%)
A	Spent ACT*DE*CON^{SM} Solution	918	0.27	918	100
B	Dilute Spent ACT*DE*CON^{SM} Solution	918	0.27	918	100

[a] ^{238}Pu retained is the difference between ^{238}Pu in the column influent and in the column effluent.

TABLE I.22 Percent of ^{238}Pu Regenerated with 1.0 M Sodium Carbonate

Column Number	Regenerant	^{238}Pu in Column Regenerant (pCi)	Percent ^{238}Pu Regenerated[a] (%)
A	1.0 M CO_3^{2-} at pH 9.0	54	6
B	1.0 M CO_3^{2-} at pH 9.0	108	12

[a] The percent ^{238}Pu regenerated was obtained by dividing the ^{238}Pu found in the column regenerant by the ^{238}Pu retained on the column (Table I.21) and multiplying by 100.

I.2.5 Summary of the Results from the Ion-Exchange Studies

It is well-known that the behavior of plutonium in solution is complex, since the system under examination is also very complex. Much of the testing performed to date has illustrated this. In addition to the ACT*DE*CON^{SM} components, the modified solution used to treat the Mound soil will contain a mixture of different species that will interact with each other and also with the ^{238}Pu (such as organic and inorganic species extracted from the sediment and colloidal material). The extent of this interaction is expected to vary with changes in, for example, pH, redox potential, and reagent concentration.

At this stage, it is not possible to suggest a suitable adsorber material for use in the preparation of MAG*SEP^{SM} particles. However, a considerable amount of valuable information has been gained from the testing described in this chapter. The testing has shown that, of the two approaches described in the introduction to this section, (i.e., an inorganic cation-exchange material and an organic anion-exchange material), the organic anion exchanger approach has been the most successful.

The testing described in Section I.2.3 has shown that the plutonium species in a fresh solution of modified ACT*DE*CON^{SM} is anionic and can be adsorbed onto an anion-exchange resin provided that the carbonate concentration is reduced. However, the resin is not selective for plutonium, and the quantity of resin required to adsorb the plutonium must be sufficient to retain all the anions in the modified ACT*DE*CON^{SM} solution as well. When the same type of resin was used to prepare MAG*SEP^{SM} particles, the quantity of particles used in the testing was insufficient to retain all the anions present in the solution, and, hence, the plutonium was not removed from solution.

The results from studies undertaken to identify the nature of the plutonium association in modified ACT*DE*CON^{SM} have shown that in excess of 80% of the plutonium is likely to be associated with the chelant in a fresh sample. A small percentage (< 20%) is associated with the humic/fulvic acid fraction of the solution.

I.3 ACT*DE*CON^{SM} Testing on Miami-Erie Canal Sediment (Task 9)

I.3.1 Introduction

As a result of the testing performed during the prior tasks of the project, a considerable amount of information has been gained relating to the behavior of plutonium in artificially spiked Mound site sediment. In the early stages of the project, contaminated Mound site sediment was not available for testing. DOE and Mound site personnel confirmed that spiking sediment to create an artificially contaminated sediment would simulate the canal sediment.

The objective of Task 9 was to demonstrate the optimum formulation, developed during Tasks 1 and 2, on contaminated sediment taken from the Miami-Erie Canal. As stated above, all prior testing had been performed using sediment from a noncontaminated area of the canal that had been artificially spiked with ^{238}Pu in the laboratory. Once the contaminated sediment was received and tested, it was evident that the ACT*DE*CON^{SM} conditions used to decontaminate artificially contaminated sediment were not effective for the plutonium in the weathered sediment. A reevaluation of the ACT*DE*CON^{SM} formulation and an investigation of the plutonium behavior had led to the development of a modified formulation for decontamination of the Mound sediment.

In order to help identify a possible cause for the reduced effectiveness of the optimum formulation, a speciation analysis was performed on both the treated and untreated Mound sediment. The speciation analysis involved sequential solvent extraction of the sediment, with increasing aggressiveness. Each solvent extraction step removed a different form of the plutonium. These forms were identified as readily available, exchangeable, organic-associated, oxides-associated, and residual. The majority of the plutonium in the contaminated untreated Mound sediment was in the organic- and oxide-associated forms, unlike the artificially spiked sediment where the plutonium was believed to be primarily in the exchangeable form. The sediment treated with the optimum formulation had reduced levels of the organic-associated plutonium, but it showed little reduction in the oxide form.

An investigation was undertaken to determine what aspect of the ACT*DE*CON^{SM} process required enhancing to enable decontamination of the sediment. Mechanical enhancements provided little benefit. Strong oxidizing and reducing reagents increased the plutonium dissolution, but also enhanced the sediment dissolution. A modified ACT*DE*CON^{SM} formulation was then developed which, when applied at a higher temperature, provided adequate plutonium removal efficiencies.

As work on all aspects of the sediment decontamination progressed, a considerable amount of information was gained concerning the behavior of the plutonium in the Mound site sediment.

I.3.2 Testing with the Optimum Formulation

An initial series of tests were performed to duplicate the work performed during Tasks 1 and 2. (Tasks 1 and 2 had been performed on artificially contaminated sediment.) This testing was to verify the ability of the optimum formulation to remove plutonium from Mound site sediment with minimal dissolution of the nonhazardous minerals.

I.3.2.1 Initial Sediment Characterization

Approximately 35 kg of plutonium-contaminated sediment from the canal were sent to the Bradtec Ltd., testing laboratory. Other than removing some of the root material and larger gravel, no other alterations were made to the sediment. Sediment samples were analyzed for potassium, nonhazardous metals (Al, Mg, Fe, and Ca), plutonium, pH, Eh and percent moisture. The results of the sediment characterization are presented in Table I.23.

The level of ^{238}Pu contamination in the Mound Site sediment samples varied from 203 to 621 pCi/g. The average of the seven analyses was 401 pCi/g. The sediment had also been analyzed by Mound Laboratory prior to shipment to Bradtec Ltd. Their analyses ranged from 367 to 581 pCi/g ^{238}Pu, with an average of 461 pCi/g.

TABLE I.23 Characterization of Mound Site Sediment

Sample No.	^{238}Pu (pCi/g)	Concentration (mg/g)					pH	Eh (mV)	Percent Moisture
		Al	K	Mg	Fe	Ca			
1	255	36.9	15.0	8.0	19.6	21.9	8.12	363	15.9
2	203	49.0	19.4	9.7	26.2	22.8	8.11	-	15.9
3	243	47.9	18.7	9.4	25.7	21.1	-	-	15.9
4	513	-	-	-	-	-	-	-	15.9
5	551	-	-	-	-	-	-	-	17.9
6	419	-	-	-	-	-	-	-	18.0
7	621	-	-	-	-	-	-	-	16.8
Average	401	44.6	17.7	9.0	23.8	21.9	8.11	363	16.6

The nonhazardous minerals and potassium concentrations present in the sediment were relatively homogeneous. The analyses indicated the following chemical concentrations: Fe, 20-26 mg/g; Al, 37-49 mg/g; K, 15-19 mg/g; Mg, 8-10 mg/g, and Ca, 21-23 mg/g. The pH of the sediment was found to be 8.1, while the Eh was 363 mV.

I.3.2.2 Laboratory-Scale Testing with Optimum ACT*DE*CON^{SM} Formulation

Duplicate samples of the Mound site sediment were washed five times using the optimum ACT*DE*CON^{SM} formulation (identified in Tasks 1 and 2) in a 20:1 ratio of solution to sediment by weight. During each wash, the sediment was combined with the wash solution, the pH was adjusted, the oxidizer was added, and the entire mixture was agitated for two hours. After each wash cycle, the wash solution was separated from the sediment by centrifuging and decanting of the liquid. The wash solution was filtered, and any residual solid that was collected was returned to the test container. After the five washes, the sediment was washed once for 30 min with deionized water. The solid was then collected and dried, and a sample sent for analysis. The DFs achieved for ^{238}Pu using the optimum formulation are presented in Table I.24. Duplicate experiments show a DF = 2.

The percent removal of nonhazardous and exchangeable minerals during this test is presented in Table I.25. The total removed from the sediment is reported as percent removal per gram mineral weight of sediment. The mineral weight is defined as the sediment weight less the moisture content and organic matter present in the sediment. Calcium was the only element that was dissolved in an appreciable amount from the sediment. Approximately 40% of the total calcium in the sediment was removed.

TABLE I.24 Results Obtained for Mound Site Sediment Washed with Optimum ACT*DE*CON^{SM} Formulation

	^{238}Pu on the Sediment (pCi/g)	
Description	Sample A	Sample B
Untreated Mound sediment	330	220
Treated Mound sediment	160	120
DF	2.1	1.9

TABLE I.25 Removal of Exchangeable and Nonhazardous Minerals from Mound Site Sediment during Testing with Optimum ACT*DE*CON^{SM} Formulation

	Exchangeable and Nonhazardous Minerals (mg/g)						
Sample	Al	Fe	K	Ca	Mg	Total	Percent Removal
A	nd[a]	nd	nd	10.7	nd	10.7	1.1%
B	nd	nd	nd	3.3	nd	3.3	0.3%

[a] nd = not detected.

I.3.2.3 Laboratory-Scale Testing with Optimum ACT*DE*CON^{SM} Formulation at 50°C

Duplicate samples of Mound sediment were washed five times at 50°C using the optimum ACT*DE*CON^{SM} formulation in a 20:1 ratio of solution to sediment by weight. The testing was performed according to the same procedure as previously described (Section I.3.2.2) with the exception that the final ACT*DE*CON^{SM} wash was continued for 24 h. The purpose of extending the fifth wash was to determine if the kinetics of decontamination was a limiting factor in the dissolution. The results from these tests are presented in Tables I.26 and I.27. Since the plutonium concentration was not significantly reduced in these tests compared to the previous tests, the kinetics of the dissolution was not considered the primary reason for ineffective plutonium removal.

I.3.2.4 Optimum ACT*DE*CON^{SM} Formulation Tests with High-Shear Mixing

Duplicate samples of Mound sediment were washed five times using the optimum ACT*DE*CON^{SM} formulation in a 20:1 ratio of solution to sediment by weight. The testing was performed with the multiple wash procedure as described earlier (Section I.3.2.2), with the exception that the first wash was subjected to high-shear mixing with a blender.

The objective of these tests was to determine if the extraction of plutonium was governed by a physical mechanism (i.e., difficulty in accessing the plutonium) as opposed to a chemical mechanism. The results from applying ACT*DE*CON^{SM} using high-shear mixing for the first wash are presented in Table I.28. The high residual plutonium on the treated sediment indicated that plutonium dissolution was not governed by a physical mechanism.

TABLE I.26 Results Obtained for Mound Site Sediment Washed with Optimum ACT*DE*CON^{SM} Formulation at 50°C

Description	^{238}Pu on the Sediment (pCi/g) Sample A	^{238}Pu on the Sediment (pCi/g) Sample B
Untreated Mound sediment	440	370
Treated Mound sediment	140	100
DF	3.2	3.7

TABLE I.27 Removal of Exchangeable and Nonhazardous Minerals from Mound Site Sediment during Testing with Optimum ACT*DE*CON^{SM} Formulation at 50°C

	Exchangeable and Nonhazardous Minerals (mg/g)						
Sample	Al	Fe	K	Ca	Mg	Total	Percent Removal
A	nd[a]	nd	nd	18.3	nd	18.3	1.8
B	nd	nd	nd	18.2	nd	18.2	1.8

[a] nd = not detected.

TABLE I.28 Results Obtained for Mound Site Sediment Using High-Shear Mixing in Conjunction with Washing with Optimum ACT*DE*CON^{SM} Formulation

Description	^{238}Pu on the Sediment (pCi/g) Sample A	^{238}Pu on the Sediment (pCi/g) Sample B
Untreated Mound sediment	394	370
Treated Mound sediment	240	232
DF	1.6	1.6

I.3.2.5 Sequential ^{238}Pu Extraction of Untreated Mound Sediment and Sediment Treated with the Optimum ACT*DE*CON^{SM} Formulation

Harwell Laboratories[10] performed five separate extractions using different leachates on duplicate sediment samples in order to identify the percentage of ^{238}Pu associated with the different sediment fractions. They also performed five extractions on duplicate sediment samples remaining after treatment with the optimum ACT*DE*CON^{SM} formulation. These tests provided information regarding which of the sediment fractions was the most difficult to decontaminate.

The ^{238}Pu activity associated with each fraction is presented in Tables I.29 and I.30 for the untreated and treated Mound sediment, respectively. The results of the speciation of the plutonium remaining on the sediment show that the majority of the residual plutonium is associated with the oxide fraction of the sediment. The second highest plutonium is associated with the organic fraction of the sediment.

As a result of these speciation tests, efforts were directed at determining reagents that can increase the oxidizing or reducing ability of the wash solution to increase the solubility of the plutonium. A series of tests were performed using strong oxidizing and reducing agents in conjunction with the optimum ACT*DE*CON^{SM} formulation to evaluate the effect on the plutonium dissolution.

I.3.3 Testing with Strong Oxidizing Agents

It is important to note at this time that the reagents used in the following tests may not be suitable for use as part of the decontamination of Mound sediment. These reagents were selected

TABLE I.29 Sequential Extraction of ^{238}Pu in Untreated Mound Sediment

	Sample A		Sample B	
Sediment Fraction	Total ^{238}Pu per Sample (pCi/g)	Percent of Total Activity (%)	Total Activity per Sample (pCi/g)	Percent of Total Activity (%)
Readily available	0.17	<1	0.082	<1
Exchangeable	1.3	<1	0.84	<1
Organic-associated	304	55	218	52
Oxides-associated	229	42	185	44
Residual	15	3	15	3.5
Total of fractions	550	100	420	100

TABLE I.30 Sequential Extraction of ^{238}Pu in Mound Sediment Treated with the Optimum ACT*DE*CON^{SM} Formulation

	Sample A		Sample B	
Sediment Fraction	Total Activity (pCi/g)	Percent of Total Activity (%)	Total Activity (pCi/g)	Percent of Total Activity (%)
Readily available	0.054	<1	0.054	<1
Exchangeable	0.41	<1	0.27	<1
Organic-associated	62	30	84	41
Oxides-associated	127	60	108	53
Residual	21	10	14	6.7
Total of fractions	211	100	205	100

and tested purely to identify the cause of the ineffective plutonium dissolution observed with the Mound sediment when compared with the results observed with artificially-contaminated Mound sediment.

Several oxidizing agents were tested in order to identify one capable of maintaining the Eh of the sediment slurry above 550 mV. Under these conditions the formation of Pu^{6+}, which is more soluble in ACT*DE*CON^{SM}, is encouraged. The same general procedure was used for this experiment except one of the following oxidizing agents — potassium permanganate, potassium dichromate, hydrogen peroxide, potassium iodate, or sodium hypochlorite — was substituted for the oxidant in the optimum ACT*DE*CON^{SM} formulation. The Eh of the solution was monitored during the reaction. The sodium hypochlorite was identified as being the most effective.

Duplicate tests were performed with sodium hypochlorite as the oxidant in the ACT*DE*CON^{SM}. Additions of oxidant were made at 10-minute intervals during the reaction period. The results from the testing with sodium hypochlorite as an oxidizing agent are presented in Table I.31. Only the treated sediment was analyzed from this test and not the wash solutions. The results can be compared to those in Table I.23.

I.3.4 Testing with Strong Reducing Agents

Two reducing agents were tested to determine if a reducing environment was more effective than an oxidizing environment. The procedure used with the reducing agents involved treating the

TABLE I.31 ^{238}Pu Remaining on Mound Sediment after Treatment with ACT*DE*CON^{SM} Formulation Utilizing Sodium Hypochlorite as the Oxidizing Agent

	^{238}Pu on the Sediment (pCi/g)	
Oxidizing Agent	Sample A	Sample B
Sodium hypochlorite	383	397

sediment with five cycles — each containing two washes. The first wash was a pretreatment with the reducing solution. The second wash solution was the optimum ACT*DE*CON^{SM} formulation at ambient temperature.

The two reducing reagents tested were (1) copper (I) oxide in 45% potassium carbonate solution and (2) 5% hydroxylamine hydrochloride solution. The copper (I) oxide in 45% potassium carbonate solution was applied for 1 h at 75°C. The 5% hydroxylamine hydrochloride solution contacted the sediment for 1 h at ambient temperature. After applying the reducing agents, each sediment was filtered and rinsed prior to applying the optimum ACT*DE*CON^{SM} solution for 1 h.

The results from the testing with the strong reducing agents are presented in Table I.32. Only the treated sediment was analyzed from these tests. It was observed that the low pH of the hydroxylamine hydrochloride solution caused a significant quantity of sediment to be dissolved during the test.

I.3.5 Testing with Oxalic Acid (Weak Reducing Agent)

The sediment was treated with five cycles containing two washes each to test the effect of a weak reducing agent. The first wash was a pretreatment step with a solution consisting of a mixture of oxalic acid and an ammonium oxalate solution. The second wash solution was the optimum ACT*DE*CON^{SM} formulation. The sediment was contacted for 18 h in the pretreatment solution at ambient temperature and then separated and washed prior to contacting with ACT*DE*CON^{SM} solution for 1 h.

TABLE I.32 ^{238}Pu Remaining on Mound Sediment after Treatment with Reducing Agents and Optimum ACT*DE*CON^{SM} Formulation

Reducing Agent	^{238}Pu on the Sediment (pCi/g)
Copper (I) oxide	55
5% Hydroxylamine hydrochloride	14

The result from pretreatment of the sediment with oxalic acid and ammonium oxalate is presented in Table I.33. Due to the low pH of the solution during the experiment, a significant quantity of sediment was dissolved. As in previous tests, only the sediment was analyzed.

I.3.6 Testing with a Modified ACT*DE*CON^{SM} Formulation

Concurrent with testing on the Mound sediment, optimization of the ACT*DE*CON^{SM} formulation for a different soil type contaminated with radionuclides and organic debris was performed.[11] The ideal application conditions identified for this soil were used on the Mound sediment. The sediment was washed five times using a modified ACT*DE*CON^{SM} solution. For each wash, the sediment was contacted for a period of 2 h. A second test sequence with the modified ACT*DE*CON^{SM} formulation was performed at 50°C. The results of the testing with modified ACT*DE*CON^{SM} reagent at ambient temperature and at 50°C are presented in Table I.34.

Since the modified ACT*DE*CON^{SM} formulation was able to remove a significant portion of the plutonium in the Mound sediment, a simulation of the in-situ ACT*DE*CON^{SM} application conditions was attempted. The effectiveness of a solution to sediment ratio of 2:1 was evaluated by washing 20-g samples of the sediment five times with 40 mL of modified ACT*DE*CON^{SM} reagent at both ambient temperature and at 50°C. The duration of each wash was 2 h. The results for each test are presented in Table I.34. Although not as effective at the higher sediment concentrations, the wash solution did show plutonium removal.

Mound sediment that had been treated with the modified ACT*DE*CON^{SM} formulation was analyzed by sequential solvent extraction by Harwell Analytical Laboratory.[10] Table I.35 shows a comparison of the results for untreated sediment, sediment treated with the optimum formulation, and sediment treated with the modified formulation.

TABLE I.33 ^{238}Pu Remaining on Mound Sediment after Treatment with Oxalic Acid/Ammonium Oxalate and Optimum ACT*DE*CON^{SM} Formulation

Reducing Agent	^{238}Pu on the Sediment (pCi/g)
Oxalic acid/ammonium oxalate	14

The results from the sequential analysis show that approximately 90% of each fraction of plutonium contained in the sediment, except the residual fraction, is removed by the modified ACT*DE*CON^{SM} formulation. The residual plutonium fraction, which is analyzed by complete digestion of the sediment, is not affected by the modified formulation.

I.3.7 Discussion

The plutonium decontamination levels achieved with artificially contaminated sediment during Task 1 of the Mound program of work, approximately 27-54 pCi/g, using the optimum ACT*DE*CON^{SM} formulation, were not achieved with the same method of application on contaminated sediment taken from the Mound site. On the Mound sediment, the residual plutonium levels were reduced to 116 pCi/g and 157 pCi/g (Table I.24) with the optimum ACT*DE*CON^{SM} formulation.

The application conditions were adjusted to determine if the plutonium dissolution was limited by kinetics or if it required a longer reaction time and/or a higher temperature. The residual ^{238}Pu during these tests was only slightly reduced, to 102 pCi/g and 136 pCi/g (Table I.26). The calcium removed during this test increased to 83% of the total calcium available, but the total mineral loss from the sediment remained less than 2%.

In order to identify a possible cause of the reduced decontamination effectiveness, untreated sediment and sediment that had been treated with the optimum ACT*DE*CON^{SM} formulation in the test described above, were treated with five separate extractants to quantify the ^{238}Pu associated with the various sediment fractions. The results, which are tabulated in Table I.29, show that the major proportion of ^{238}Pu is associated with the organic fraction (approximately 54%) and the oxide fraction (approximately 43%); approximately 3% of the ^{238}Pu present in the Mound sediment is identified as residual. Examination of the results from the treated sediment (Table I.30) shows that between 67% and 76% of the organically bound ^{238}Pu and between 38%

TABLE I.34 ^{238}Pu Remaining on Sediment after Treatment with the Modified ACT*DE*CON^{SM} Formulation Under Various Test Conditions

Treatment Description	^{238}Pu on the Sediment (pCi/g)
Modified ACT*DE*CON^{SM} formulation at ambient temperature	97
Modified ACT*DE*CON^{SM} formulation at 50°C	30
Modified ACT*DE*CON^{SM} formulation at ambient temperature and a 2:1 solution to sediment ratio	157
Modified ACT*DE*CON^{SM} formulation at 50°C and a 2:1 solution to sediment ratio	108

TABLE I.35 Comparison of Plutonium Concentrations from Sequential Extraction Analysis of Sediments Treated with Modified ACT*DE*CON^{SM} Formulation

	Activity (pCi/g)		
Sediment Fraction	Untreated Sediment[a]	Optimum Formulation Treated Sediment[a]	Modified Formulation Treated Sediment[b]
Readily available	0.12	0.05	<0.01
Exchangeable	1.1	0.34	0.05
Organic-associated	260	73	7.3
Oxides-associated	207	118	24
Residual	15	18	24
Total of fractions	498	209	55

[a] Results obtained from the average of two samples, dry weight.

[b] Results from the analysis of sediment from repeated testing (described in Section I.4), dry weight.

and 47% of the oxide-bound ^{238}Pu were removed with the optimum ACT*DE*CON^{SM} formulation. As expected, the residual ^{238}Pu remained undissolved. These results identified the major problem as the dissolution of oxide-bound ^{238}Pu.

In order to access the ^{238}Pu bound within the oxides or organic species in the sediment, a series of tests was conducted using a high-shear mixing vessel for the first contact of the sediment with the ACT*DE*CON^{SM} solution. Use of this method improved plutonium dissolution during testing with other sludge mixtures.[11] The results of these tests with Mound sediment, however, showed little improvement.

Plutonium (VI) complexes are known to be more soluble in aqueous systems than plutonium (IV) complexes. The possibility existed that the dissolved iron in the ACT*DE*CON^{SM} solution was preventing the oxidation of Pu (IV). Several oxidizing agents were examined for their ability to maintain the solution Eh above 550 mV during the testing. It is in this region that Pu^{6+} is formed in preference to Pu^{4+} in a carbonate system. Sodium hypochlorite was chosen as a possible effective oxidizing agent. The results of the tests, however, showed the decontamination to be adversely affected. The DFs obtained were approximately 1, and the residual ^{238}Pu concentration was approximately 390 pCi/g.

Sediment contains a variety of spinels that are composed of various ratios of iron, manganese, and aluminum. These spinels can also bind significant quantities of ^{238}Pu. Reducing conditions are often necessary to break the spinel and release the ^{238}Pu. Two reducing agents were applied as part of the ACT*DE*CON^{SM} process. It should be noted that these reagents would not be applied to the sediment during the decontamination of the Mound site, but they were used only to determine if the decontamination could be improved. The reagents tested were copper (I) oxide and 5% hydroxylamine hydrochloride. The results showed a considerable increase in the decontamination factor. The ^{238}Pu contamination on the treated sediment was reduced to approximately 55 pCi/g with copper (I) oxide and to 14 pCi/g with hydroxylamine hydrochloride. The exceptionally low result using hydroxylamine hydrochloride may be due, in part, to the low pH of the solution, which caused approximately 50% of the sediment weight to be lost by dissolution. The testing with a reducing agent and in particular, with copper (I) oxide, showed that the combination of a reducing step and an ACT*DE*CON^{SM} wash effectively decontaminated the sediment.

An oxalic acid/ammonium oxalate treatment was also tried with ACT*DE*CON^{SM}. The extractant was used in the sequential extraction procedure to remove the oxide-bound plutonium, while ACT*DE*CON^{SM} was used to remove the organically bound plutonium. The results from this test were a significant improvement in ^{238}Pu removal. However, due to the low pH of the solution, 50% of the sediment weight was lost by dissolution.

In solutions of high ionic strength, organic acids (such as humic acids) will "unravel" and consequently will expose the bound plutonium. Previous testing with sediment/sludges[16] showed that an increase in carbonate concentration caused a significant improvement in the plutonium dissolution. Thus, an ACT*DE*CON^{SM} formulation was developed that incorporated this information. Mound site sediment was tested with the "modified" formulation at both ambient temperature and at 50°C (to further enhance the decontamination). The results from these tests showed a significant improvement in ^{238}Pu decontamination. The residual ^{238}Pu was reduced to 97 pCi/g for the test performed at ambient temperature. When the temperature was increased to 50°C, the residual ^{238}Pu was reduced to 30 pCi/g.

The application of modified ACT*DE*CON^{SM} formulation to Mound sediment was repeated at ambient temperature and at 50°C using a 2:1 ratio of solution to sediment. The reduction in the plutonium concentration demonstrated that the contaminant can be removed under these conditions. Therefore, it is possible to use a recirculating application technique with a low solution to sediment ratio to remove the plutonium from Mound sediment.

Analysis of the major nonhazardous and exchangeable minerals present in the sediment, before and after application of ACT*DE*CON^{SM}, revealed that the most significant weight loss was due to the change in calcium concentration. This loss was most likely due to an exchange reaction with sodium used in the ACT*DE*CON^{SM} reagents. High concentrations of sodium and carbonate may significantly influence the properties of the cleaned sediment and adversely affect plant regrowth. In addition, sediments with a high sodium content frequently swell or disperse, greatly reducing the hydraulic conductivity or permeability of water. Clay particles deflocculate and plug the sediment water flow channels, inhibiting water percolation through the sediment. Decreased permeability can interfere with the drainage required for normal salinity control and with aeration necessary for plant growth.

At high pH, clay forms stable deflocculated suspensions where flocculation is prevented by the electric double layer caused by the hydrated cations. The thickness of this double layer is inversely proportional to the electrolyte concentration in the sediment solution and decreases with increasing valence of the involved cations. Therefore, sodium will induce a thicker layer than calcium, and potassium is believed to induce a thinner layer than sodium.

Detrimental effects on sediment quality caused by the reagents and/or the shearing action of the mixing tools may be rectified at the end of the process by using a rinse cycle containing calcium sulfate (gypsum) to replace the calcium and improve the sediment stability. Alternatively, given the low solubility of gypsum, the sediment could be neutralized with sulfuric acid, which would dissolve some of the calcite. Additives (such as compost) that increase the hydraulic conductivity of the sediment, have shown interesting results associated with dewatering times and may be beneficial.

into testing of Mound sediment only when the difference between spiked and actual sediments was

I.3.8 Conclusions

Experimental work in the program has led to the following conclusions:

- ^{238}Pu in the contaminated sediment from the Mound site is primarily associated with the oxide- or organic-associated fractions of the sediment. This association is in contrast to the artificially contaminated sediment used in Tasks 1 and 2, where the ^{238}Pu contamination was mainly exchangeable. Decontamination of the Mound sediment with the optimum ACT*DE*CON^{SM} formulation was not as effective as decontamination of the spiked sediment.

- Successful decontamination of the Mound sediment was achieved by treatment with a strong reducing agent followed by ACT*DE*CON^{SM} in a five-wash cycle. The ^{238}Pu contamination was reduced to 14 pCi/g, with a high dissolution of the sediment.

- Effective decontamination of the sediment was also achieved by treatment with a modified ACT*DE*CON^{SM} solution of high ionic strength. Residual ^{238}Pu contamination was reduced to 97 pCi/g at ambient temperature and to 30 pCi/g at 50°C.

- Decreasing the solution to sediment ratio from 20:1 to 2:1 and contacting the sediment with a modified ACT*DE*CON^{SM} formulation resulted in a residual ^{238}Pu concentration of 157 pCi/g at ambient temperature and 108 pCi/g at 50°C.

TABLE I.36 Decontamination of Mound Sediment Pretreatment Characterization

Sample Description	^{238}Pu Concentration (pCi/g)	Percent Moisture
Untreated Sediment	729	20.3
	428	20.0
	918	20.2
Average	692	20.2

water. The treated sediment samples were oven-dried at 60°C for 24 h. A sample from each

TABLE I.37 Mass Balance for the Removal of ^{238}Pu with the Modified ACT*DE*CON^{SM} Formulation

Sample	^{238}Pu in Treated Sediment pCi/g	^{238}Pu in Treated Sediment Moisture-Corrected[a] pCi/g	Total ^{238}Pu in Treated Sediment (pCi)	Total ^{238}Pu in Solution (pCi)	Total Available ^{238}Pu (pCi)	Calculated Initial ^{238}Pu on Sediment[b] (pCi/g)
A	56.7	45.2	339.7	4,058	4,398	734.1
B	70.2	56.0	420.6	5,178	5,599	934.5
C	56.7	45.2	339.8	3,950	4,290	715.8
Average	61.2	48.8	366.7	4,395	4,762	794.8

[a] These values were corrected for the average percent moisture (20.2%) present in the initial sediment sample.

[b] Calculated for the dry weight of the sediment (average sample weight 6.0 g).

A range of filtration systems was evaluated for possible application in the integrated demonstration, in-situ and/or ex-situ applications. These systems are in commercial use in the mineral processing industry, where substantial efforts have been put into dewatering slurries over many years to improve ore yields.[12] Some of these methods have been adapted for use in other sediment remediation work. An investigation was undertaken to determine which method would provide the best results for the Mound sediment.

I.4.3.1 Fixed Screens/Sieves

Fixed screens and sieves are generally available only down to 35 μm. Sizes less than 35 μm are achievable, but only using matched plate technology with reduced slurry throughput. Trials with sieves in the laboratory under gravity drainage (to simulate in-situ drainage) showed that for a slurry poured directly onto the sieve, initial passage of the slurry through the sieve was followed by blinding, which resulted in no drainage at all in the sediment inner layer between the sieve and the slurry.

Johnson Well screens were reviewed for possible use at pilot and full-scale in-situ application, because they have an improved sieve/screen design. The finest available Johnson Well screen is 35 μm. Because the earlier results showed that small pore holes were easily blinded with the sediment, this method of filtration was determined to be unsuitable.

I.4.3.2 Filter Press

Prior experience has shown that filter presses are not efficient with a high fraction of material less than 10 µm. In addition, long-term operation of filter presses requires higher levels of maintenance, when compared to other competing processes.

I.4.3.3 Moving Screen Filters

The design of moving screen filters offers the potential to continuously present a clean filtration membrane to the process slurry, thus reducing the tendency for fine particles to blind the membrane. The original design for this type of filter was the drum filter, which has been in use in the minerals-processing industry for over 80 years. This type of process is slower than the filter press, as vacuum is used as the driving force, but this filter design allows continuous operation. The conventional drum filter uses an air blast to clean the filter membrane before reimmersion in the slurry. More advanced designs utilize water-jet washes for more efficient removal of solids from the filter membrane.

I.4.3.4 Evaluation of Filter Membranes

Several filter membrane materials were evaluated for use with a horizontal bond filter. Evaluation trials were performed with a Büchner funnel assembly, using standardized quantities of slurry with the different filter media. The particle size distribution of the Mound sediment indicated that a needle felt filter membrane would be more appropriate than a mesh filter. One grade of mesh filter was tested (FE 3350, Scandiafelt Mesh AB), along with three needle felt grades (all supplied by P&S Filtration Ltd., via Delkor Ltd.). The membrane with the best performance, quantified by rate of filtrate removal from the slurry and filtrate clarity, was AMP 47 needle felt filter. Filter belts of this membrane material were subsequently made for use with a demonstration-scale horizontal bond filter.

I.4.4 Large Laboratory-Scale Filter Test Equipment

A large laboratory-scale, sediment-processing, filtration evaluation system was built that allowed ACT*DE*CON^{SM} treatment of larger quantities of sediment. The equipment was used for demonstrations and for preparing sediment for testing various types of filtration methods. The equipment processed sediment taken from a nonradioactive section of the Mound site.

The large laboratory-scale system test equipment was designed to process sediment under batch conditions. At the start of the processing cycle, sediment was placed in the mixing vessel. A mixing tool was used to inject and blend the ACT*DE*CON^{SM} solution into the sediment. The speed of the tool was controlled in both its vertical movement and its rate of rotation. Washed sediment was pumped to the filter belt as a slurry to remove the wash solution. The filter cake was returned to the mixing vessel, where it was washed with additional ACT*DE*CON^{SM} solution.

The framework of the equipment is enclosed with clear plastic panels to protect the operator from moving parts. Each panel also contains an emergency stop button for safe equipment shutdown. Several panels are removable for ease of access and contain interlocks that prevent equipment operation if the panels are removed. A high efficiency particulate air (HEPA) filter is part of the system to control dust.

The sediment-processing area of the system has a vessel with a volume capacity of approximately 10 L. The sediment is initially placed in the bottom of the vessel. A mixing blade, designed to simulate commercially available sediment-mixing equipment, injects and blends the ACT*DE*CON^{SM} into the sediment. A screw-drive platform controls the vertical movement of the blade. Limit switches halt and reverse the direction of the blade. The switches are preset for the maximum upper and lower transverse of the mixing blade for the mixing area. When the platform reaches a switch, the drive motor reverses the platform's direction. A second upper switch allows for removal of the blade from the vessel, but it prevents the platform from reaching the top of the drive screws and damaging the equipment. The screw drive platform also controls the speed of the vertical movement. A second drive unit controls the speed of the rotating blade.

When the mixing blade contacts the sediment, the injection pump is switched on to begin injection of the ACT*DE*CON^{SM}. After the required volume of ACT*DE*CON^{SM} has been delivered, the injection pump is switched off. The system is allowed to operate for the required amount of time for the ACT*DE*CON^{SM} to contact the sediment.

Separation of the sediment from the ACT*DE*CON^{SM} solution requires the use of solid/liquid separation technology that has not currently been identified for the pilot-scale testing and field application. The high fines content of the silt/clay sediment, combined with the high salt content of the wash solution, causes a slow settling of the solids. The use of standard filtration technology produces extended filtration times or plugging of filter media. A study was performed to provide a preliminary evaluation of different additives that could be used to aid filtration. Concurrently a study evaluated various filter technology and filtering materials (Section I.4.3).

The use of a vacuum belt filter with AMP 47 needle felt filter cloth provided the best results for the demonstration equipment. The sediment was slurried from the mixing vessel onto the filter belt, where it passed over a vacuum that removed the liquid from the sediment. The dewatered cake was constantly scraped from the belt and returned to the vessel for additional washes.

I.4.5 Filtration Equipment Demonstration

A demonstration horizontal bond filter was used for dewatering the slurry. Initial work with the system showed that filtration rates were not providing acceptable solid/slurry separation. A hydrocyclone was added to the slurry feed system, which improved the filtration efficiency. However, this addition resulted in the loss of sediment in the (recirculating) overflow from the hydrocyclone (nominally, the < 3 µm fraction). The belt wash system also contributed to sediment loss. Although this problem is difficult to correct on a pilot scale, for full-scale applications, the hydrocyclone overflow and the belt wash liquid would be slowly fed onto the filter belt precoated with the coarse cut from the hydrocyclone, thereby minimizing sediment loss.

The wash/sediment mixture, as it was slurried to the filter, passed through the hydrocyclone. The feed slurry entered the hydrocyclone tangentially under pressure. Because of the high centrifugal forces, particles coarser than the "cut point" migrated into a primary vortex adjacent to the wall and moved downward. Finer particles migrated into a secondary upward-moving vortex and were discharged with most of the water out the overflow. The coarser particles were discharged onto the belt filter.[12]

A commercial-scale design would use several hydrocyclone stages to lay down a layered cake, using the sediment itself to effectively generate its own precoat layers without flocculant or other additions. This technology allowed testing on a large laboratory-scale, but the technology would be unsuitable for a pilot or full field application. The main benefit of the technology is that it did not require other sediment additives, which could hinder the ACT*DE*CON^{SM} chemistry.

I.4.6 Sediment Preparation

In order to show the operation of the equipment and to prepare the clean sediments for the regrowth study, the large-scale-system test equipment was set up and operated in SELENTEC's Atlanta facility. The testing was performed in accordance with Bradtec Ltd. test procedure TP 23.02.01.[13] Two kilograms of clean sediment, which had been air dried, was placed in the bottom of the mixing vessel. ACT*DE*CON^{SM} solution, prepared as the modified formulation, was mixed with the sediment in a 4:1 solution to sediment ratio (assuming the sediment had a density of 2 g/mL). Five wash cycles were performed with contact times of 2 h each followed by two water washes. The filter system was used to process the first batch of sediment. However, due to the large sediment loss to the hydrocyclone and filter belt wash, additional batches were separated from the solutions by allowing the sediment to settle and decanting the liquid. The washed sediment was then allowed to air dry.

I.5 Commercial-Scale Magnetic Particle Recovery Tests (Task 11)

I.5.1 Introduction

Demonstration of the magnetic particle recovery system was performed on a commercial-scale system at the Clemson Technical Center (CTC). The commercial-scale system was built to provide a practical method to demonstrate MAG*SEP^{SM} technology through recovery of the particles by magnetic filtration.

Electromagnetic filtration (EMF) is a commercially available technique for the removal of suspended, magnetically susceptible material from a process flow stream. The filters are extremely efficient and are rated as being capable of removing over 95% of the particulate magnetite present in a process stream. The EMF unit has a design that contains a matrix of magnetizable steel balls. The magnetic field in the matrix when energized is greater than 5 kG, with localized areas of higher magnetic intensity where the balls touch. When the filter matrix becomes loaded with magnetically susceptible material, the EMF unit is bypassed and the matrix de-energized and flushed.

The proposed concept for the process application was to remove the plutonium from the sediment by washing with ACT*DE*CON^{SM} solution. The solution would subsequently be collected and treated with MAG*SEP^{SM} particles that had been coated with an adsorber with a high selectivity for plutonium. After an appropriate contact time, the MAG*SEP^{SM} particles and adsorbed plutonium would be removed from the ACT*DE*CON^{SM} solution by the use of a magnetic filtration system.

During the sediment wash cycle, it is anticipated that sediment fines will become entrained in the ACT*DE*CON^{SM} solution during extraction from the sediment. Thus, the effect that sediment fines would have on the magnetic filter's ability to retain MAG*SEP^{SM} particles required additional investigation.

The results described in this section were obtained from work performed under "Mound Task 11 Test Plan, Revision 3".[14]

I.5.2 Evaluation of Magnetic Filter System

The magnetic filter system was operated to demonstrate two objectives: (1) to quantify the amount of magnetic and paramagnetic sediment fines retained by the filter and (2) to determine the efficiency of the magnetic filter for removal of MAG*SEP^{SM} particles as a function of flow rate and sediment concentration in the feed.

To achieve the first objective, the properties of the sediment slurry were observed as the slurry passed through the magnetic filter. Magnetic and paramagnetic material in the slurry will become trapped in an energized magnetic filter. This material, if not removed, will be collected with the MAG*SEP^{SM} particles. Tests were performed to determine whether premagnetic filtration of magnetic and paramagnetic materials in the Mound sediment is required prior to MAG*SEP^{SM} particle injection into the mixture. Prefiltering the sediment can minimize the collection and concentration of these materials with the particles.

The test method involved passing a sediment slurry through the system and determining how much sediment was retained in the magnetic filter. A 5 wt% slurry of sediment was pumped through the system at various flow rates. After each test run the magnet was isolated, degaussed, and back-flushed. The flush mixture from each run was collected and dried, and the quantity of sediment removed by the magnet, as a percent of the total initial amount of sediment in the slurry, was calculated.

The results showed that for a 5 wt% slurry mixture, the quantity of magnetic and paramagnetic sediment retained on the filter at a high flow rate (16 gpm) was 1.3%, while 4.5% is retained at a low flow rate (4 gpm). The lower the flow rate, the higher the percentage of sediment retained by the filter. These results show that extracted ACT*DE*CON^{SM} wash solution will require a premagnetic filtration step, prior to the addition of MAG*SEP^{SM} particles. A prefiltration step will reduce the amount of sediment collected with the MAG*SEP^{SM} particles and the quantity necessary to be handled as waste.

Thus, during full-scale system design, a decision will have to be made with regard to the processing of the wash solution in batches — prefiltering to remove the magnetic and paramagnetic sediment from the entrained sediment or having a continuous-flow system requiring two magnetic filter systems.

A second objective of the tests with the magnetic filtration system was to determine the particle removal efficiency, on a single pass, as a function of sediment concentration and flow rate. The purpose of these tests was to determine if a single pass through the magnetic filter, recycling through the magnetic filter with multiple passes, or having two magnetic filters in series for MAG*SEP^{SM} particle removal is necessary. The required removal efficiency for the particles is greater than 99%.

Tests performed with a particle/water mixture showed greater than 99% of the particles were collected on the magnet in a single pass (as determined by drying and weighing the sediment removed from the magnetic filter). Attempts to repeat this result with particles in a sediment slurry mixture were unsuccessful, because a small amount of sediment adhered to the particles.

In order to demonstrate that greater than 99% of the particles were retained by the magnetic filter from the sediment slurries, a different analysis method, based on the use of a rare-earth magnet, was developed to examine the filter effluent. A cylindrical magnet, containing several rare-earth magnetic disks, was used to collect any MAG*SEP^{SM} particles that had passed through the magnetic filter. The magnet was placed in a plastic sleeve and swirled through the drum that contained the effluent mixture. After swirling the magnet in the drum for a 2-min time period, the plastic sleeve was examined to determine if any particles were not retained by the magnetic filter and were subsequently captured by the cylindrical magnet.

To check and verify that this method would remove any particles present in the mixture, a sample of MAG*SEP^{SM} particles equal to the fault condition (0.1% of the initial quantity) was mixed into the drum and removed by the same technique. The results conclusively showed that if the magnetic filter had retained less than 99% of the particles, this analysis method would detect the remainder in the effluent mixture.

I.5.3 Test Conditions

The purpose of the work performed under this task was to demonstrate the performance of the magnetic filter and its ability to recover 99% of the MAG*SEP^{SM} particles. The information below describes the test conditions and the results obtained.

The flow rate per cross-sectional area of the commercial-scale EMF unit is the same value throughout the size range of commercially available as well as "custom-built" B & W Nuclear Technologies EMF units. The design parameters for the magnetic coil of each EMF, including the commercial-scale unit, are such that the field strength is 5 kG. In addition, the volume (capacity) of each EMF is such that operating cycle times will be the same for any size filter, given the same concentration of magnetic material in the stream.

I.5.3.1 Test Solution Preparation

It was determined that water was sufficient to slurry the sediment and that an ACT*DE*CON^{SM} solution was not required.[15] The ACT*DE*CON^{SM} solution to be used in sediment treatment applications at Mound will contain approximately 1-3% chemical loading. The chemical constituents will dissolve a small amount of mineral ions, but the fluid properties of the water will not be altered enough to affect the recovery of MAG*SEP^{SM} particles. By preparing the sediment slurry mixtures with water, the slurry handling requirements were minimized.

I.5.3.2 Perform Particle Recovery Tests for Different Flow Rates and Sediment Entrainment Concentrations

Due to the magnitude of sediment handling required for each test run, the number of runs performed was decreased to three flow tests at the 5% sediment slurry and two at 1%. The 5%

sediment slurry (worst-case) test runs were conducted at "full flow," "half flow" and "quarter flow" (16, 8, and 4 gpm, respectively). The 1% sediment slurry runs were conducted at 16 and 4 gpm. These test parameters bracketed the envelope of expected operating conditions. A duplicate test run at full flow and 5% sediment concentration (most severe conditions) was performed as a check of the results.

The 5% sediment slurry was prepared by weighing 5.02 kg of sediment that had been predried and sieved to remove the greater-than-300 µm fraction. The sediment was mixed with demineralized water to a volume of 25 gal. In accordance with the equipment operating manual,[16] the slurry was recirculated through the EMF system at 4 gpm for 30 min to remove the magnetic and paramagnetic portion from the sediment. The filter was isolated and back-flushed. A total of 227.15 g of magnetic and paramagnetic sediment was collected. The collected sediment represented approximately 4.5% of the initial sediment weight.

I.5.3.3 Analyze Filter Effluent Samples for MAG*SEP^{SM} Particle Concentration

The effluent mixture was analyzed for the presence of MAG*SEP^{SM} particles according to the test procedure.[14] The method basically involved adding 10 g of MAG*SEP^{SM} particles to a pretreated slurry of sediment. The sediment slurry had been pretreated to remove the natural magnetic and paramagnetic material. The mixture was then passed through the filter, and the effluent tested for MAG*SEP^{SM} particles by swirling a strong rare-earth magnet in the collection drum.

After examining the effluent for particles, a verification of the process was performed by adding a 0.1-g sample of MAG*SEP^{SM} particles to the effluent mixture and repeating the above retrieval method. This quantity of MAG*SEP^{SM} is equivalent to 0.1% of the initial amount added to the slurry. The particles were added to demonstrate that this small amount of particles could be detected by this analysis method. The results obtained are shown in Table I.38.

I.5.3.4 Analyze Backwash for Presence of Sediment Fines in Backwash Solids

The EMF's ability to recover MAG*SEP^{SM} particles from water was demonstrated in previous MAG*SEP^{SM} commercial-scale equipment tests.[17] In the tests conducted with a sediment slurry, visual examination of the particulate in the filter backwash showed that a small amount of sediment fines were retained along with the particles. Performing a mass balance was not practical due to handling loss in separating the sediment from the MAG*SEP^{SM} particles and the tolerances of the fault condition. Thus, the results of this subtask offer little quantitative data on MAG*SEP^{SM} particle retention in the filter.

TABLE I.38 MAG*SEP^{SM} System Efficiency Test Results

Slurry Mixture (wt%)	Flow Rate (gpm)	Weight (g) MAG*SEP^{SM} Particles Added Initially	MAG*SEP^{SM} Particles Retrieved from Filter Effluent	MAG*SEP^{SM} Particles Added for Validity Check	MAG*SEP^{SM} Particles Retrieved from Validity Check
5	16	10.02	<0.001[a]	0.102	0.071
5	8	10.00	<0.001[a]	0.102	0.084
5	4	10.00	<0.001[a]	0.102	0.091
5[b]	16	10.01	<0.001[a]	0.103	0.078
1	16	10.03	0.017	0.102	0.069
1	4	10.01	0.010	0.101	0.052

[a] Quantity of particles detected in filter effluent was less than the level of detection used to measure the sediment.

[b] Duplicate sample.

I.5.3.5 Evaluate Results and Determine the Operating Conditions to be Used for Commercial-Scale Testing

It can be concluded from the results of these tests that a magnetic "prefiltration" system will be necessary to remove magnetic and paramagnetic components of the sediment from the wash solution prior to injecting MAG*SEP^{SM} particles into the mixture. The prefiltration system must be operated at a relatively low flow rate to maximize removal of these sediment materials.

According to the results presented in Table I.38, the EMF system retained greater than 99% of the MAG*SEP^{SM} particles from the sediment mixture on a single pass through the filter at various flow rates and sediment concentrations. Operation of the particle recovery system should be at a maximum flow rate to minimize the amount of sediment fines that adhere to the particles. Sediment fines retained by the magnet are difficult to separate from the particles and tend to complicate the particle regeneration process and increase the waste volume for disposal. On the basis of the test conditions, these conclusions and recommendations are valid for sediment concentrations up to 5% by weight, over a flow range of one-quarter to full rated flow.

I.5.4 Conclusions

The testing demonstrated that, due to the amount of sediment material that is retained by the magnetic filter, a separation system is required to remove the magnetic and paramagnetic sediment from the ACT*DE*CON^{SM} wash solution prior to injection of the MAG*SEP^{SM} particles. The results also showed that retention of the MAG*SEP^{SM} particles by the magnetic filter is sufficient to require only a single magnetic filtration system to achieve greater than 99% particle removal efficiency.

I.6 Conclusions

The accomplishments for each task are summarized as follows:

*Task 1 Optimization of the ACT*DE*CON^{SM} Formulation for Spiked Mound Sediment*

Using artificially contaminated Mound sediment, 11 experimental formulations were examined for the ability to reduce the ^{238}Pu contamination level to an acceptable value using the lowest chemical loading. A successful formulation was found and is referred to as the optimum formulation.

Task 2 Evaluation of the Dissolution of Nonhazardous Minerals

In order to appraise the effects to the treated sediment following application of the ACT*DE*CON^{SM} process, an evaluation of the dissolution of the most abundant elements present in the sediment was made. This evaluation was performed on the treated sediment after contact with the optimum ACT*DE*CON^{SM} formulation and, later in the program, after contact with the modified ACT*DE*CON^{SM} formulation. In both evaluations the percent removal of nonhazardous minerals was approximately 2% of the nonorganic fraction (less than the target 10%).

Task 4 Ion-Exchange Material Studies
Task 5 Magnetic Particle Optimization Studies
Task 6 Magnetic Particle Regeneration Studies

The initial objectives of these tasks were to (1) identify a suitable ion-exchange material from which to prepare MAG*SEP^{SM} particles; (2) optimize the MAG*SEP^{SM} particle contact time and solution to particle ratio; and (3) evaluate the regeneration conditions of the particles. The ion-exchange material identified at an early stage of the program was ineffective for the chemical conditions required to decontaminate the weathered Mound sediment. As a result, the tasks were combined, and emphasis was placed on the identification of the nature of the plutonium in a spent ACT*DE*CON^{SM} solution. This latter investigation indicated that the plutonium can be removed with an anion-exchange resin but not in a manner selective for plutonium. A speciation study using DEAE cellulose suggested that in excess of 80% of the ^{238}Pu was associated with the chelant and less than 20% was associated with the sediment organic material.

Task 8 Laboratory-Scale Integration Test with Mound Site Sediment

As a result of the differences encountered between artificially spiked sediment and contaminated Mound sediment, this task was combined with Task 10 .

Task 9 Laboratory-Scale Dissolution Tests with Mound Site Sediment

The plutonium on artificially spiked Mound sediment, although initially thought to behave in the same way as the plutonium on Mound sediment, behaved quite differently. Reformulation of the ACT*DE*CON^{SM} solution resulted in the decontamination of the weathered Mound sediment to an acceptable level.

Task 10 Laboratory-Scale Integration Test with Mound Site Sediment

The purpose of this task was to perform an initial evaluation of the full process application. A system that simulated the conditions for field application was designed and constructed. Noncontaminated sediment, which was processed through the system, demonstrated the difficulties that will be incurred with an in-situ approach. Due to the high percentage of silt and clay in the sediment, percolation of the ACT*DE*CON^{SM} solution through the sediment was impractical. Additional investigations into alternative means of solid/liquid separation are required.

Task 11 Commercial-Scale Magnetic Particle Recovery

The MAG*SEP^{SM} particle recovery testing demonstrated that particles were efficiently recovered from sediment slurries of up to 5 wt% solids. Less than 0.1% of the particles were detected in the process effluent. This result indicated that only one pass through a magnetic filter unit will be required to retrieve >99% of the particles.

The analysis of the Mound sediment showed a high concentration of magnetic and paramagnetic material. In order to minimize the quantity of material that would have to be handled as secondary waste, the magnetic and paramagnetic material will have to be removed from the process slurry before treatment with MAG*SEP^{SM}. Since no testing was performed on contaminated sediment with the MAG*SEP^{SM} system, a determination of the amount of plutonium associated with the magnetic and paramagnetic material will have to be performed. If the plutonium is adequately removed during the wash process, this material could be returned to the canal.

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Mound-ACT*DE*CON^{SM} Feasibility Study, Phase II: Final Report

Chapter II

Task 3 Plutonium Mobility Studies in Soil/Sediment Treated with ACT*DE*CON^{SM}

by

M. Cristina Negri, Kent A. Orlandini, and Jerry McNally
Argonne National Laboratory[†]

December 1994

[†] Negri and McNally are affiliated with Argonne's Energy Systems Division and Orlandini is affiliated with Argonne's Environmental Research Division.

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Chapter II

Task 3 Plutonium Mobility Studies in Soil/Sediment Treated with ACT*DE*CON℠

by

M. Cristina Negri, Kent A. Orlandini, and Jerry McNally
Argonne National Laboratory

Summary

The ACT*DE*CON℠ process extracts plutonium (Pu) from contaminated soils/sediments by means of a series of washings with a blend of chemicals, among which are a chelating agent and an oxidant. At the end of the process, the Pu level in the soil is expected to be lowered to 25-30 pCi/g. The radionuclide still present in the soil at the end of the treatment is strongly immobilized in or onto soil particles, minimizing the risk of its percolation to the aquifer and/or uptake by vegetation. In Task 3 of the Mound Phase II project, the residual Pu mobility was investigated in terms of the distribution coefficient (K_d). In addition, a chemical/physical characterization of the Mound soil/sediment before and after the ACT*DE*CON℠ treatment and a preliminary germination study were carried out to provide the necessary information for the K_d studies and to serve as a starting point for the postponed regrowth studies.

Preliminary studies evaluating the K_d on ACT*DE*CON℠-treated vs. untreated Mound soil, obtained from Bradtec Ltd., indicated that rainwater was more aggressive (constituting the worst-case scenario) in removing Pu from the soil than discharge (basin) water. In more comprehensive studies, six batches of contaminated soil from Mound were treated simultaneously with the ACT*DE*CON℠ process. Some batches of the treated soil were amended with a standard fertilizer treatment of compost and nutrient and brought to a pH of 8.5. The treated, treated/fertilized, and nontreated soils were incubated at 18°C for 90 days. At four different times during the incubation period, a small aliquot of soil was retrieved from each of the batches and contacted with rainwater for six days to determine the Pu solid /liquid distribution and K_d.

Results indicated that a higher total amount of Pu was leached from the nontreated soil, probably as a consequence of the higher content of available/exchangeable Pu in the nontreated soils as compared to the treated one. Treated/fertilized soils showed Pu leaching at intermediate levels between treated and untreated soils, at least for the first 30 days of incubation. K_d values at the beginning of the incubation period were significantly lower in the untreated and treated-fertilized soils compared to the treated-only soil, but at 90 days the values were essentially equal for the three different soils. The chelating agent was detectable only in treated, nonfertilized soil, and at levels comparable to the set limit values.

Germination tests showed a sharp phytotoxicity to watercress (*Lepidium sativum*) of saturation extracts from treated soil at several dilutions. Toxicity may be attributed to the high salinity levels as well as to the presence of organic compounds. These compounds may have originated from the breakdown of naturally existing organic matter by the ACT*DE*CON^{SM} treatment or by the development of anaerobic flora in the structureless, anoxic, treated soil. More in-depth evaluation of the regrowth aspects will be necessary once the final ACT*DE*CON^{SM} formulation is defined.

II.1 Purpose and Background

The ACT*DE*CON^{SM} process extracts plutonium (Pu) and uranium from contaminated soils/sediments by means of a series of washings of the contaminated material with a blend of chemicals, among which are a chelating agent, an oxidizing agent, and carbonates. A series of rinsing cycles follows the washing phase, with the purpose of completely removing the ACT*DE*CON^{SM} chemicals together with all the mobilized radionuclides. At the end of the process, the activity level of the soil is expected to be reduced to approximately 25-30 pCi/g (1 pCi = 10-12 Ci) from an average initial level of 500 pCi/g. It is important that the radionuclide still present in the soil at the end of the treatment be strongly immobilized in or onto the soil particles, minimizing the risk of its percolation into groundwater and/or uptake by vegetation in significant amounts.

The mobility of plutonium, which determines its uptake by plants and its leaching into groundwater, is dependent on time, microbial metabolism, and soil chemical/physical conditions. Chemical speciation of the Pu remaining in the soil, accompanied by distribution coefficient studies, can be very informative in predicting plant uptake.

Task 3 of Phase II of the Mound-ACT*DE*CON^{SM} Feasibility Study deals with the investigation of the mobility of the Pu still present in Mound-contaminated soil after treatment with the ACT*DE*CON^{SM} chemicals.

The purpose of the experiment considered here is to evaluate Pu mobility before and after a treatment that has drastically affected the chemical form of the Pu and its bonding to soil particles. Traces of some of the reagents might still be in the soil, even after the best technological rinsing performance, thus maintaining some of the Pu in a mobilized form. Possibly the residual Pu might be less strongly attached to the soil particles after the treatment, as a result of incomplete action by the chemicals. The chelating agent is (slowly) biodegradable and leachable; therefore, an increased mobility of Pu due to the presence of the chelating agent is of temporary interest. After such degradation, the treated and untreated substrates should tend to show more similar behavior, unless microbial activity and changes in the chemical/physical conditions of the soil following restoration of "normal" status (pH, redox potential) induce measurable differences.

The problem of ensuring that all the mobilized plutonium and the chelating agent are out of the system at the end of the process has been recognized in recent months as a materials handling issue, dependent on the hydraulic characteristics of the final "soil material"; it will be addressed as such in other tasks of the project. For this task, Pu mobility as a function of the chemical form of the Pu and its bonding into the soil matrix is the research priority, rather than the potential presence of Pu in mobile forms from incomplete rinses due to technical problems. In the case of the present experiment, it is assumed that the soil has been cleaned of the process chemicals to the greatest degree achievable.

In Task 3 experiments, we investigated the

- *Mobility of the Pu* not removed by the ACT*DE*CON^{SM} treatment: its potential for being taken up by vegetation and/or to be leached through the sediment profile into the aquifers, and the

- *Possible presence of unwanted residual amounts* of ACT*DE*CON^{SM} chemicals in the soil after the treatment (a provisional limit of <15 mg/kg soil has been set).

Distribution coefficient (K_d) studies are used to assess the adsorption/desorption of radionuclides onto soil/liquid phases. Such studies have been widely used in the determination of sorption properties of sediments, soils, and several "pure" materials, such as special clays, rocks, etc. They have also been utilized in assessing the potential desorption of radionuclides from contaminated sediments to water. K_d is defined as the ratio of the concentration of the element in the soil (dry basis) to the concentration of the element in the aqueous phase that is in equilibrium with the soil (expressed in milliliters per gram [mL/g]).

Typically, K_d studies are carried out in batch or column mode. The K_d value may be influenced by the solid/liquid ratio, the size and type of filter used in separating the liquid phase, the ionic strength and pH of the liquid used, the grain size of the solid fraction, and the presence and amount of other competing ions in the extracting solution. In the present case, the needed information is related to differences found among various soil conditions, rather than to the assessment of absolute values. Therefore, the influence of the testing conditions should be of lesser importance, provided that the conditions are maintained the same throughout the test. However, a worst-case scenario was chosen in selecting the solid/liquid ratio and the contact liquid (rainwater vs. discharge water).

Analysis of soil particle size and visual observation from attempted solids separation have shown that the Mound soil has a very low permeability* and that its fine fraction is very difficult to separate from the liquid phase. Because column studies might not be able to provide leachate at all, and derived long retention times might confound Pu leachability and the presence of the chelating agent during the initial time after treatment, a batch-contact method was preferred for this study.

Preliminary data from previous tasks suggested a need to supply the treated soil with amendments in relatively large amounts to achieve the needed soil revegetation after the cleanup. Therefore, the effect on Pu mobility of amendments and structure-improving materials was also investigated in this study. Addition of organic matter has been controversially related to both increased immobilization of Pu and potential solubilization by chelation by soluble fractions of decaying organic matter.

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* Rogers reports a water permeability of 0.1-1.0 m/yr in Mound clay (1975).

II.2 Materials and Methods

II.2.1 Preliminary Studies

Preliminary studies were conducted on treated and untreated soils obtained from Bradtec Ltd.; these soils were derived from the conduction of the ACT*DE*CON^{SM} demonstration as part of Task 8/10. The purposes of the preliminary K_d determination were to obtain an estimated value of K_d, to better focus the work of the following studies, and to select the type of contact water that would prove most aggressive in mobilizing Pu (thereby, constituting the "worst-case scenario" for the following experiments).

Samples used for the preliminary K_d determination were Bradtec Ltd. No. 02546 (untreated contaminated Mound soil, at 20% moisture and 486 pCi/g ^{238}Pu [AEA-Harwell data]) and Bradtec Ltd. No. 02549 (treated Mound soil, dried, at 56.7 pCi/g ^{238}Pu [AEA-Harwell data]). Two aliquots of a sample, each equivalent to 0.300 g of dry soil, were placed into their own 1000-mL plastic bottles; 300 mL of Mound rainwater was added to one aliquot and 300 mL of discharge (basin) water was added to the other. The lids were closed, and the water-soil suspension was stirred with a magnetic stirrer for one week. Samples of approximately 50 mL each were taken at 24 h, 48 h, and one week; these samples were filtered with a 0.45-µm millipore filter membrane and analyzed for Pu according to standard methods reported elsewhere (Nelson and Lovett 1978; Wahlgren and Orlandini 1982; and Nelson and Orlandini 1986).

Given the ample margin of differences (orders of magnitude) between the soil and the water activity, and the derived small significance of potential differences between results obtained by Bradtec Ltd. (Harwell, Task 8/10 determinations) and by ANL, determination of Pu in the soil was not deemed necessary, and K_d values were calculated by using Harwell's analytical data for the soil provided by Bradtec Ltd.

II.2.2 Plutonium Distribution Coefficient Studies

Following the preliminary studies, contaminated moist soil obtained from Mound (Mound samples #9402626 and 9402627) was thoroughly mixed in a plastic tray, cleared of evident stones and root debris, and sampled for Pu and moisture analysis. Nine aliquots of moist soil, each equivalent to 40 g of dry soil, were accurately weighed and placed in nine plastic, 1000-mL centrifuge bottles, numbered from 1 to 9.

While bottles 7, 8, and 9 were sealed and left aside as controls, the other six bottles of soil were subjected to ACT*DE*CON^{SM} treatment according to the Bradtec Ltd. procedure: ACT*DE*CON^{SM} solution was heated to 50°C on a hot plate, and when the temperature was stable at the set value, 800 mL of the solution was added to each bottle. The bottles were then placed in individual stirred water baths and stirred gently at 50± 2°C. Stirring was sufficient to keep the soil mass suspended in the ACT*DE*CON^{SM} liquid. After the initial mixing, the pH and temperature values were checked and recorded, and the oxidizing agent was added to each bottle. After the 2 h of contact, the bottles were removed from the bath and centrifuged at 2000 rpm for 15 min. Once the solids were firmly separated from the liquid phase, the liquid was removed, and the solids were washed four more times according to the same procedure. The liquid phase (contacted ACT*DE*CON^{SM}) was measured in a calibrated cylinder, sampled (25 mL from each bottle were collected in a 2000-mL container), and the rest was discarded in the radioactive waste container.

After the fifth ACT*DE*CON^{SM} wash, the solids were slurried with 300 mL of deionized water, mixed for 10 min, and then centrifuged for 30 min at 2000 rpm. A proportional (3% of sample) 10-mL sample of the rinse for each bottle was placed in the 2000-mL container with the 25-mL sample from each wash to obtain a weighed composite sample of all the extractions and rinses.

At the end of the procedure (first K_d contact at day 4 from soil washing), a composite sample of the solids was prepared by retrieving 1 g of material from each of the six bottles and mixing them together with a glass rod. A 1-g aliquot of the mixture was dried at 105°C to determine the moisture level, and it was analyzed for Pu. Two other aliquots of the mixture were weighed to obtain the equivalent of 0.300 g of dry soil, and each was placed in a 500-mL glass flask. In a similar manner, a cumulative sample of the three control soil samples was prepared and equivalent aliquots were also weighed and placed in flasks. To each flask, 300 mL of Mound rainwater was added; the flasks were then sealed with parafilm, and their contents were gently stirred for six days. After six days, an aliquot of the soil suspension was filtered with a 0.45-µm millipore membrane and sampled for Pu analysis; the remainder was forwarded to Argonne National Laboratory (ANL) Analytical Chemistry Laboratory for chelant high-pressure liquid chromatography (HPLC) analysis.

Three days after completion of the ACT*DE*CON^{SM} treatment, the soil in bottles 4, 5, and 6 was individually slurried with 80 mL of deionized water, neutralized with 0.1 N sulphuric acid to a pH of 8-8.5, and then centrifuged for 16 min to remove the excess liquid (pH of the supernatant liquid was 8.35). To each bottle, 3 g of dry yard-waste compost, 10 mg KH_2PO_4, 26 mg urea, and 0.5 mL of mixed, nonchelated microelements were added. In order to determine the amounts of fertilizer amendments added, agronomical analyses were performed on clean Mound soil before and after treatment with ACT*DE*CON^{SM} simulant (see Appendix II.A). After accurate mixing and rechecking of the soil moisture level, all nine bottles were placed in the incubator at 16-18°C.

At 19, 30, and 90 days from the beginning of the experiment, an aliquot of soil from each bottle was weighed (0.300 g of dry soil) and contacted for six days with 300 mL of rainwater, according to the previously described method, to determine the second, third, and fourth K_d value series. Chelant analysis was performed only on the samples taken at 4 and 19 days, at the direction of DOE, given the fact that these series already provided concentration levels within the preset maximum acceptable levels of 15 mg/L. The analytical method adopted for the chelant determination was a modified version of the method of Bergers and de Groot (1994) (see Appendix II.B), and the analyses were performed by the ANL Analytical Chemistry Laboratory.

Preliminary studies on the phytotoxicity of the treated soil are described in Appendix II.C. An in-depth evaluation of the regrowth capabilities of treated soil will be necessary after the final ACT*DE*CON^{SM} formulation is defined.

II.3 Results

Results from the preliminary studies are summarized in Table II.1. The Pu balance in the soil/ACT*DE*CON^{SM} samples after the washing process is indicated in Table II.2, and the results of the K_d studies are summarized in Tables II.3 to II.7 and in Figures II.1 to II.4.

The results of the statistical evaluation of the Pu dissolutions and K_d data (Bonferoni's multiple means comparison test) are summarized in Tables II.6 and II.7. These tables report all comparisons between two of the obtained mean values that resulted statistically significant at the probability level of 95% ($\alpha = 0.05$) or 99% ($\alpha = 0.01$).

The preliminary K_d evaluation conducted on ACT*DE*CON^{SM}-treated soil gave important information to shape the subsequent experiment. In general, a higher dissolution of plutonium was obtained with rainwater than with basin water. The effect was more evident in untreated soil. Treated soil consistently released less Pu than untreated soil, and this smaller value might be confounding the differences between the waters used. Equilibrium was probably reached within 24 h, but the data appear not to vary significantly in the three filtration times. K_d varied between 7×10^4 and 1.2×10^6, with most of the data lying within the 10^5 range.

At the analysis of variance (ANOVA), both K_d values and dissolution values (fCi/L) obtained in the following full-scale experiment showed significant differences ($\alpha = 0.01$), induced by the type of treatment and by the time of contact. Further statistical testing (Bonferoni's multiple means comparison test) showed that these differences were attributable to a number of direct comparisons between mean values of Pu dissolution and K_d (see Tables II.6 and II.7).

Untreated soil gave dissolution values (Pu dissolution in fCi/L values, Table II.3) that were significantly different ($\alpha = 0.01$) and were approximately 10 times higher than those obtained with treated samples. Significant differences were also found between dissolution from treated fertilized and untreated soil samples at 19, 30, and 90 days. The anticipated trend towards increased dissolution of plutonium in treated/fertilized soil vs. treated soil is confounded by the variability of the data and is not confirmed by the statistical analysis. The same can be said about the dissolution from treated soil at all contact times. The higher degree of dissolution obtained from untreated soil at 30 and 90 days is, on the other hand, confirmed as significantly different from the lower dissolution levels obtained during the first two contacts.

TABLE II.1 ^{238}Pu Activity and Derived K_d on Bradtec Ltd. Mound Soil Samples Contacted with Rainwater or Basin Water (preliminary K_d determination) (1 fCi = 10^{-15} Ci)

	Untreated Soil		Treated Soil	
Item	Rainwater	Basin Water	Rainwater	Basin Water
Pu Activity (fCi/L in water)				
at 24 h	5,304	1,227	88	132
at 48 h	6,885	1,454	213	142
at 1 week	4,000	1,000	374	45
Derived K_d				
at 24 h	$9.4 \times 10^4 \pm 0.9$	$4 \times 10^5 \pm 1$	$6.4 \times 10^5 \pm 1.1$	$4.2 \times 10^5 \pm 1.3$
at 48 h	$7.0 \times 10^4 \pm 0.7$	$3.4 \times 10^5 \pm 0.8$	$2.6 \times 10^5 \pm 0.7$	$4 \times 10^5 \pm 1.3$
at 1 week	$1.3 \times 10^5 \pm 0.06$	$5.0 \times 10^5 \pm 0.5$	$1.5 \times 10^5 \pm 0.2$	$1.25 \times 10^6 \pm 5$
pH at 24 h	7.06	7.74	7.10	7.43

TABLE II.2 ^{238}Pu Balance in Washing Contaminated Mound Soil with ACT*DE*CON^{SM} (data on composite samples)

	^{238}Pu in Dry Soil (pCi/g)	Total ^{238}Pu (nCi)	Moisture in Solids (%)	DF[a]
Untreated soil[b]	844	202.6	24.2	-
Pu extracted in ACT*DE*CON^{SM}	767.7	184.1	n/a[c]	-
Treated soil	77.3	18.5	56.1	10.91

[a] DF (decontamination factor) = Pu in untreated soil/Pu in treated soil.

[b] Value calculated by adding extracted Pu to residual Pu in soil.

[c] n/a = not applicable.

TABLE II.3 Plutonium Extraction in the Four K_d Contacts

	Plutonium Extracted (fCi/L)		
Days	Treated Soil	Treated/Fertilized Soil	Untreated Soil
4	137[a]	n/a	1,879[a]
	(4)[b]		(1,197)
19	112[c]	292[c]	3,964[c]
	(51)	(26)	(1,369)
30	325[c]	856[c]	11,193[c]
	(145)	(140)	(678)
90	514[c]	488[c]	5,891[c]
	(237)	(187)	(704)

[a] Mean value of two replications.

[b] Numbers in parentheses give the standard deviation.

[c] Mean value of three replications.

TABLE II.4 Plutonium Distribution in Solid/Liquid Fractions as K_d Values

	K_d		
Days	Treated Soil	Treated/Fertilized Soil	Untreated Soil
4	566,490[a]	n/a	563,777[a]
	(14,673)[b]		(359,284)
19	794,857[c]	266,404[c]	228,109[c]
	(356,247)	(22,863)	(66,045)
30	287,441[c]	92,045[c]	86,193[c]
	(167,406)	(15,738)	(39,801)
90	170,737[c]	172,300[c]	144,752[c]
	(66,825)	(55,293)	(18,516)

[a] Mean value of 2 replications.

[b] Numbers in parentheses give the standard deviation.

[c] Mean value of three replications.

TABLE II.5 Chelant Concentration in each Liquid-Phase K_d Contact Replication[a]

	Chelant Concentration (mg/L)		
Days	Treated Soil	Treated/Fertilized Soil	Untreated Soil
4	6	n/a	< 5
	5		< 5
19	16	< 5	< 5
	13	< 5	< 5
	11	< 5	< 5

[a] Detection limit was 5 mg/L.

TABLE II.6 Bonferoni's Multiple Means Comparison Test: Significant Comparisons on fCi/L Data[a]

Item	T4	T19	T30	T90	TF19	TF30	TF90	U4	U19	U30	U90
T4	/	-	-	-	-	-	-	-	b	c	c
T19		/	-	-	-	-	-	-	b	c	c
T30			/	-	-	-	-	-	b	c	c
T90				/	-	-	-	-	-	c	c
TF19					/	-	-	-	b	c	c
TF30						/	-	-	-	c	c
TF90							/	-	-	c	c
U4								/	-	c	b
U19									/	c	-
U30										/	c
U90											/

[a] T = treated soil, TF = treated/fertilized soil, U = untreated soil. Number represents days from treatment.

[b] Significant at $\alpha = 0.05$.

[c] Significant at $\alpha = 0.01$.

TABLE II.7 Bonferoni's Multiple Means Comparison Test: Significant Comparisons on K_d Data[a]

Item	T4	T19	T30	T90	TF19	TF30	TF90	U4	U19	U30	U90
T4	/	-	b	c	b	c	c	-	b	-	c
T19		/	c	c	c	c	c	-	c	c	-
T30			/	-	-	-	-	b	-	-	-
T90				/	-	-	-	c	-	-	-
TF19					/	-	-	b	-	-	-
TF30						/	-	c	-	-	-
TF90							/	c	-	-	-
U4								/	b	c	c
U19									/	-	-
U30										/	-
U90											/

[a] T = treated soil, TF = treated/fertilized soil, U = untreated soil. Number represents days from treatment.

[b] Significant at $\alpha = 0.05$.

[c] Significant at $\alpha = 0.01$.

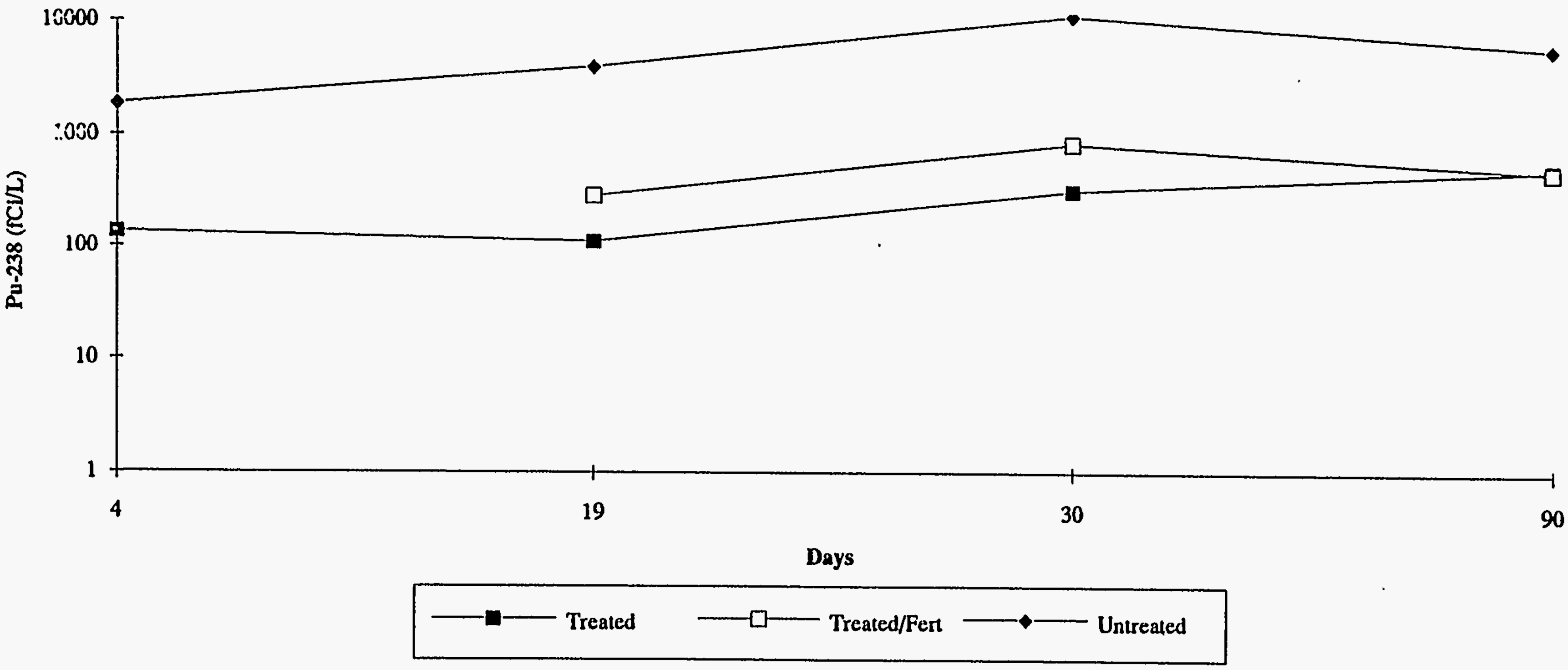

FIGURE II.1 Plutonium Extraction in the Four K_d Contacts, Mean Values, fCi/L

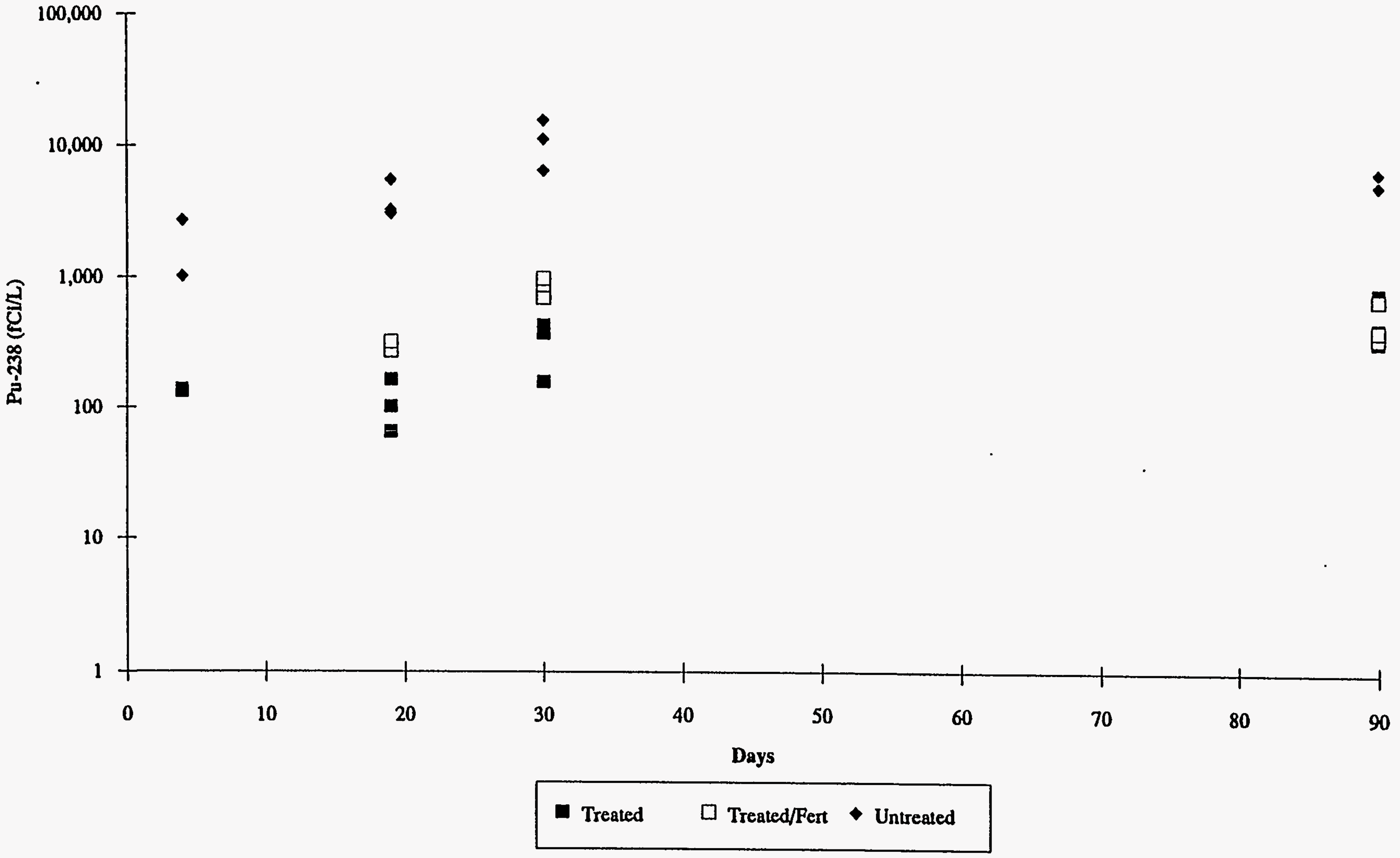

FIGURE II.2 Plutonium Extraction in the Four K_d Contacts, fCi/L, All Replications

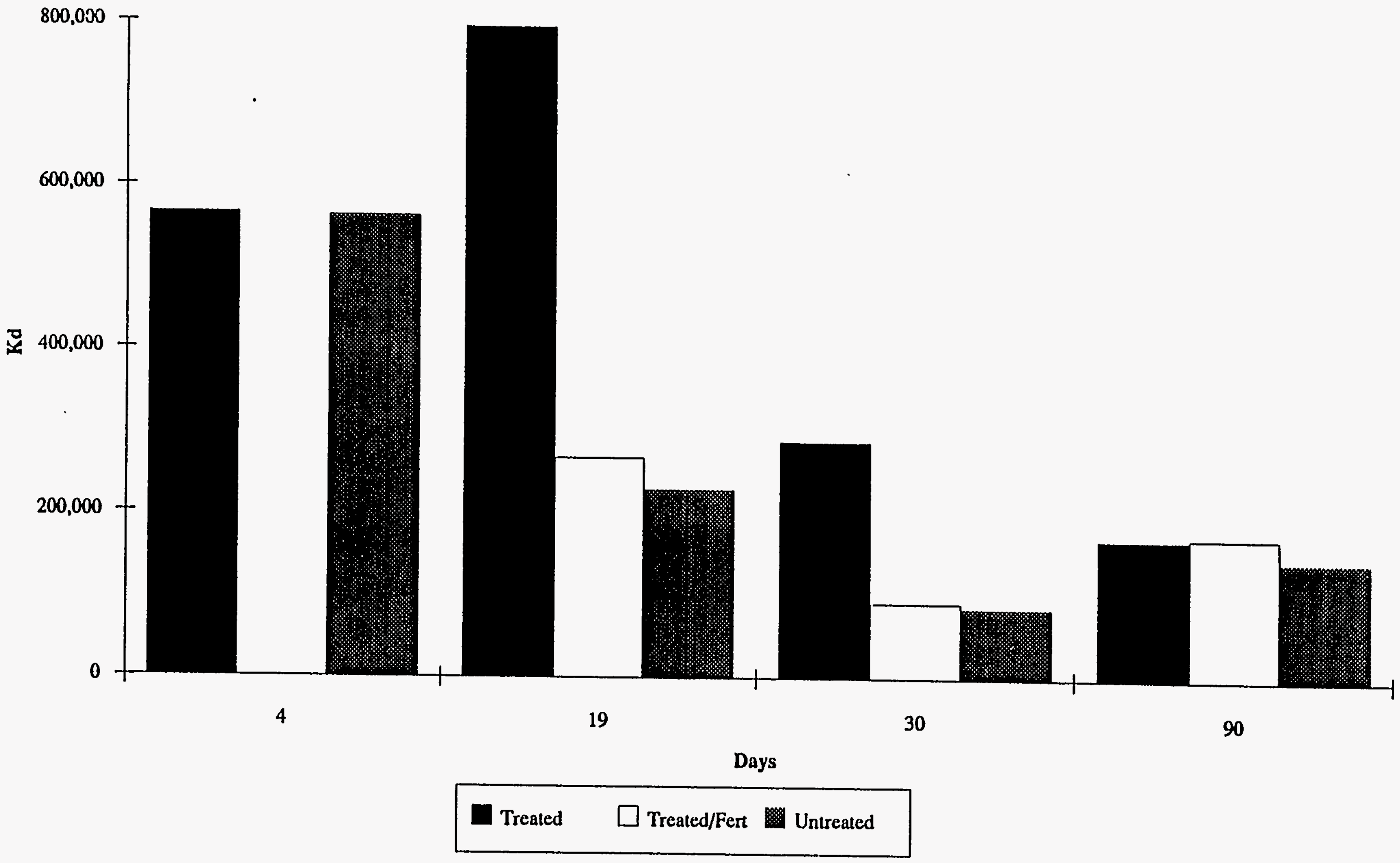

FIGURE II.3 Plutonium Distribution in Solid/Liquid Fractions, as K_d, Mean Values

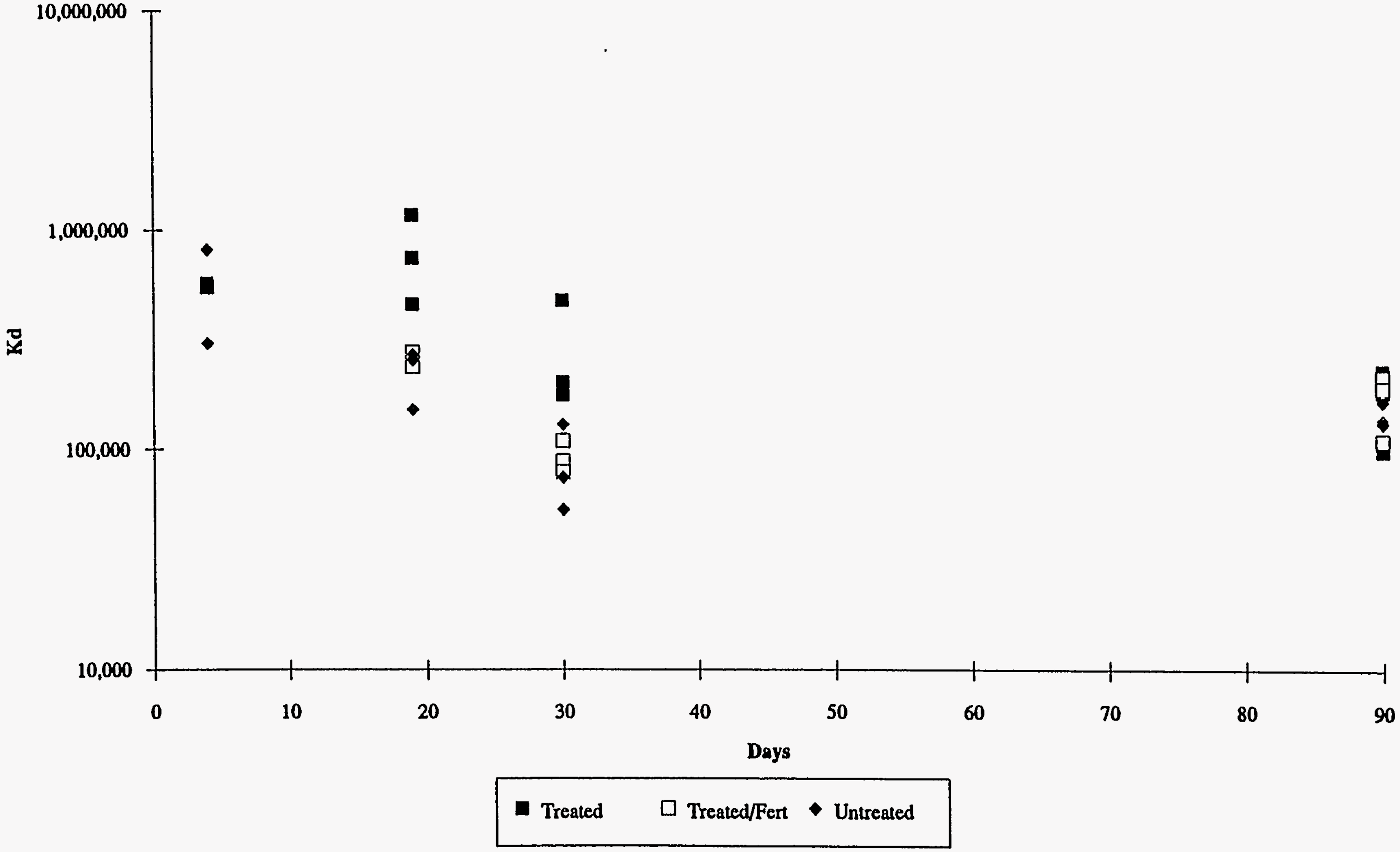

FIGURE II.4 Plutonium Distribution in Solid/Liquid Fractions, K_d, All Replications

K_d values (Tables II.3-II.4) at 4 days from the soil treatment showed no significant difference induced by the ACT*DE*CON^{SM} treatment. At 19 days, however, K_d values obtained for treated soils were significantly higher than those obtained for treated/fertilized and untreated soils. These differences decreased with time and were not statistically significant at 90 days from the treatment. To further confirm this trend, treated and untreated soils had K_d values at 4 days that were statistically higher than those obtained at 30 and 90 days. Treated/fertilized soil had K_d values not statistically dissimilar from those of untreated soil at 19, 30, and 90 days. Differences between treated and treated/fertilized soil were significant only at 19 days.

Chelant analysis by HPLC was conducted on the filtered liquid from the first two contacts of the soil with ACT*DE*CON^{SM}. As expected, no chelant was detected in the samples derived from the untreated soil. Treated soil samples showed traces of chelant at 4 days and more evident values at 19 days; considering the dilution made and assuming that all the chelant was extracted from the soil, at 19 days, the levels of chelant in soil were comparable with that (15 mg/kg) assumed as a limiting value. Treated/fertilized soil showed no detectable presence of chelant at 19 days, in contrast to soil that had been only treated.

II.4 Discussion and Conclusions

In preliminary K_d studies, Pu dissolution at different equilibration times was tested. Some variation of the dissolution levels was found, and it is uncertain whether equilibrium was reached at 24 h. Therefore, the decision was made to adopt a six-day equilibration time for the subsequent experiments. Although the term K_d was adopted in this report for simplicity, equilibrium was not demonstrated, so a better definition of the ratio obtained would be R_d (distribution ratio).

The total amount of Pu that was leached by rainwater from the contaminated, untreated, Mound soil in this experiment proved to be consistently higher (about ten times) than the amount extracted by rainwater from the same soil after it was treated with ACT*DE*CON^{SM}. This result can be explained by the fact that treated soil was poorer in Pu, as well as by the sequential extraction findings by Bradtec (1994), which showed that the ACT*DE*CON^{SM} treatment removed most of the readily available and exchangeable Pu, leaving the most strongly bound Pu in the soil. A sequential extraction technique was used by Bradtec, during Task 9 investigations in this project, to determine Pu associations in contaminated Mound soil samples before and after treatment with the modified ACT*DE*CON^{SM} formulation. Results suggested that, in the untreated soil, about 0.2% of the Pu is readily available/exchangeable, more than 50% is bound to the organic matter, another 40-43% is associated with the oxides, and 3% is insoluble. In the sequential extractions, the reagents used were calcium chloride, tetrasodium pyrophosphate, oxalic acid-oxalate, and total acid dissolution, respectively. After the ACT*DE*CON^{SM} treatment, the residual Pu was 0.1% exchangeable, 13% organic-associated, 43% oxide-associated, and 43% insoluble. If the same percentages were adopted for the samples used in this experiment, approximately 1,700 fCi/g soil would be exchangeable from untreated soil, and 770 fCi/g from treated soil; such values are comparable, in a gross sense, with the dissolution data obtained.

K_d values of treated and untreated soil were initially comparable and tended to decrease in both soils (i.e., to increase Pu mobilization into the liquid phase) with time. Over short intervals, the ACT*DE*CON^{SM} treatment seemed to induce a higher K_d, but the difference with that of untreated soil decreased over longer time intervals, and at 90 days the K_d values in treated and untreated soils were equal. The fertilization treatment induced a significant decrease in the K_d and made the values for treated/fertilized soil comparable with those obtained for untreated soils. In other words, the fertilization increased the ratio of Pu that was extracted by the rainwater (and filtered through the 0.45-µm filter) to the level for untreated soil. At the end of the testing period, the data were equal for the three different soil conditions; thus, in terms of time interval, the fertilization shortened the time needed for the residual plutonium in treated soil to reach K_d values analogous to those of untreated soil. In no case did the treated soil (with or without fertilization) have K_d values lower than those of untreated soils, so a higher relative mobility of the residual plutonium is not suspected.

The concentration of chelant measured in the first two contacts was within the limited range of values set as maximum acceptable concentration, although a comparison is not completely valid, because no specific analytical method was indicated to support the established limit value. At

19 days, chelant was present in measurable amounts in treated soil but not in treated/fertilized soil; this fact supports a hypothesis of either degradation of chelant or nonreversible adsorption of chelant onto soil particles/organic amendment.

The lower chelant concentration found at 4 days might be explained by the existing fluctuation among samples or by the longer time that the four-day aqueous sample was preserved prior to analysis (for increased analytical accuracy, all samples were analyzed at the same time); the wait might have allowed partial degradation of the chelant to occur in the water. In this case, a faster degradation of chelant in water rather than in soil would be necessarily assumed. The time-constrained effect of chelating agents and the derived inferred degradation is not new to the literature: in plant uptake experiments, where an increase in uptake was found if the radionuclide was supplied as chelated with DTPA or EDDHA, decreasing radionuclide mobility was found after the first period by Hale and Wallace (1970; cited in Harris 1989), who noticed a lower uptake of DTPA-Americium by plants after 30 days, and by Romney et al. (1976,1978,1985; cited in Harris 1989), who found that the chelator-increased radionuclide plant uptake diminished over successive harvests.

In any case, the absence of chelating agent in cases where a higher Pu extraction was found suggests that the residual chelating agent was not an element of concern under these conditions for increased Pu activity in the contact water. The data on chelating agent, however, are too few to allow a definite conclusion, and confirmation will be necessary once the final ACT*DE*CON^{SM} formulation has been defined. These data should therefore be used as indicative values of what is possibly found in the soil after the ACT*DE*CON^{SM} treatment under the best available conditions (lab-scale work allows for much more precise operational conditions than pilot- or field-scale operations).

The results obtained in this series of contacts are consistent with those usually found in the literature for natural ecosystems. Literature data show a wide range of adsorption/desorption K_d values in soil/sediment solutions. Ranges vary between 10 and 10^6 mL/g, depending on soil characteristics, total radionuclide concentration or activity, and whether the experiment is an evaluation of environmental samples or a simulation experiment (Sanchez et al. 1982; Radioactive Waste Management Center 1990). In the case of simulation experiments, the leaching system adopted (batch, column) and the use of artificially spiked solutions/solids are of fundamental importance in determining the K_d. Usually, the lower K_d values were from those tests in which samples were artificially spiked, generally at significantly higher activity levels (μCi, rather than pCi). In nature, plutonium K_d values for marine, riverine, and lacustrine environments have been reported as rather constant at 1×10^4 to 1×10^6 (IAEA 1985; Nelson et al. 1987; Sanchez et al. 1982).

Plutonium mobility has been evaluated in the literature by distribution coefficient studies, as well as by speciation and sequential chemical extraction studies and by analyzing plant uptake after cultivation in Pu-contaminated soil. Plutonium mobility is reported to vary with the physical, chemical, and microbiological characteristics of the soil (Romney and Davis 1972; Francis 1973;

Nishita et al. 1978). Wang and Yu (1992) conducted batch U-Th desorption studies, using alkaline soils (pH approximately 8.5); the desorption of the radionuclides increased as the pH of the contacting solutions was lowered, and humic acid additions were able to increase the desorption from soil by at least a factor of four, compared to that for deionized water.

Reasons for increased dissolution of radionuclides from soil (amended or not) have been connected by various authors with such factors as pH and Eh changes, the direct presence of natural organic matter (such as decaying roots, which has complexing characteristics that prevent the readsorption of Pu onto soil particles) (Romney et al. 1970, cited in Francis 1973), and the production (induced by microbes/fungi) of extracellular metabolites able to complex Pu (Wildung and Garland 1987). Nelson et al. (1987), in a study of natural waters/sediment K_d values, describe natural dissolved organic compounds (DOC) (such as humic materials) as important complexing agents for many metals in surface waters; they state that the formation of water-soluble, metal-organic complexes could be responsible for a decrease in adsorption of Pu in sediments associated with waters rich in DOCs.

Some of the effects of varying soil conditions have been studied in the literature relating Pu mobility to its accumulation in plant tissues, as is the case in the evaluation of the effects of soil amendments and fertilization. Garland et al. (1974) reported an increased plant Pu uptake following incubation of a Ritzville soil (pH 6.8) with carbon and nitrogen to provide maximum microbial activity. Rediske et al. (1955, cited in Francis 1973) reported a more than three times greater uptake of Pu from acidic rather than alkaline soil, and Romney et al. (1976, cited in Harris 1989) found that addition of sulfur was able to increase significantly the uptake of americium and Pu-239-240 .

In the present investigation, the fertilization treatment consisted of lowering the pH to a more vegetation-acceptable level (pH in fertilized soil was 8.5, compared to higher levels in unfertilized, treated soil) and in restoring some of the organic matter lost with the ACT*DE*CON^{SM} washes. Urea and potassium phosphate, as well as micronutrients, were supplied to ensure the potential for microbial life and the utilization of the organic matter supplied. Both pH decrease and the presence of some microbial activity might be responsible for the temporarily increased plutonium mobility.

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Appendix II.A:

Characteristics of Clean Mound Soil before and after the ACT*DE*CON^{SM} Treatment and Characteristics of the Spent ACT*DE*CON^{SM} Effluent

Appendix A:

Characteristics of Clean Mound Soil before and after the ACT*DE*CON^{SM} Treatment and Characteristics of the Spent ACT*DE*CON^{SM} Effluent

In order to evaluate fertilization and amendment requirements in the treated soil, agronomical and physical analyses were performed on uncontaminated soil samples taken from the Miami-Erie Canal approximately two miles north of the contaminated site. Such soil is believed to have characteristics similar to those of the contaminated soil.

A representative sample of spent ACT*DE*CON^{SM} solution was tested in order to characterize the waste generated by the process. In this case, also, the process simulated the treatment on uncontaminated Mound soil.

Results of the analyses are summarized in Tables II.A.1 and II.A.2. The analytical methods adopted are also listed.

TABLE II.A.1 Results of Chemical Analysis of Untreated and Treated Uncontaminated Mound Soil and of the Spent ACT*DE*CON^{SM} Effluent (representative sample of five washes and three rinses per Bradtec Ltd. procedure)

Item	Untreated Soil	Treated Soil	Spent ACT*DE*CON^{SM} Effluent
pH	7.8	10.2	9.24
Organic carbon (%)	3.6	2.6	n/a[a]
Cationic exchange capacity (CEC) (cmol/kg)	35.7	n/a	n/a
Total phosphorus (mg/kg)	1183	8.1	n/a
TKN (mg/kg)	2523	8.03	n/a
Bray PO_4 (mg/kg)	10.2	n/a	n/a
Extractable bases (mg/kg)			n/a
Ca			
Na	5914	181	
Mg	21	5806	
K	648	138	
	155	194	
DTPA extractable (mg/kg)		n/a	n/a
Fe	50		
Zn	14.3		
Cu	20.2		
Cd	0.73		
Ni	1.08		
Total solids (%)			8.7
Fixed solids (ash)(% dry)			16.7

Item	Untreated Soil (mg/kg dry soil)	Treated Soil (mg/kg dry soil)	Spent ACT*DE*CON^{SM} Effluent (mg/L)
Total elements			
Cd	11.7		0.17
Fe	26,928		41.34
Ni	51		0.67
Zn	216		0.73
Cu	264		0.8
Mg	n/a		29.52
Pb	99.4		1.62
Cr	97.5		0.97
Hg	0.22		0.003
As	78		9.36
Mn	n/a		3.55
Al	n/a		5.92

[a] n/a = not applicable.

TABLE II.A.2 Texture Analysis/Hydrometer for the 24-hour Method[a]

Particle size	µm	Percent
Medium, coarse, and very coarse sand	>100	12.5
Very fine sand	63 to 100	0
Coarse silt	32 to 60	4.5
Medium silt	17 to 31	11.2
Fine silt	9 to 16	19.4
Very fine silt	5 to 8	31.2
Coarse clay	3 to 4	0
Medium clay	1 to 2	33.12
Fine clay	< 1	0
Texture class	silty clay loam	

[a] Average of two replications; clean, untreated soil.

Reference Analytical Methods

pH: *Methods of Soil Analysis*, Part II, No. 9 (Part 2) in the series *Agronomy*, A.L. Page (editor), American Society of Agronomy, Inc., Soil Science of America, Inc., Madison, Wisc., 1982, pp. 208-209.

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TOTAL SOLIDS AND FIXED SOLIDS: Gravimetric method at 105°C and 550°C.

Appendix II.B:

HPLC Method for Analysis of the Chelant Agent in Water

Appendix II.B:

HPLC Method for Analysis of the Chelant Agent in Water

The analysis method followed was a slightly modified version of that published by Bergers and de Groot in *Water Research* 1994, 28, 639-642.

Solutions:

1. Chelant stock standard: 1 g/L chelant solution is made by dissolving 1.27 g Na_2H_2-chelant•$2H_2O$ in 1 L of water. Calibration standards were prepared from this solution by dilution.
2. Iron (III) chloride: A 1.75 g/L solution was prepared by dissolving 175 mg $FeCl_3$•$6H_2O$ in 30 mL glacial acetic acid and diluting to 100 mL with water.
3. HPLC mobile phase: The mobile phase was a 0.03M acetate/acetic acid buffer of pH 4 with an ion pairing reagent. It was prepared by dissolving 2.5 g sodium acetate in 800 mL water and adding 9.7 mL glacial acetic acid; 7.3 mL of a 55% aqueous solution of tetrabutyl ammonium hydroxide was added, and the volume was brought to 1 L with water.

Procedure:

Before analysis, 100 µL of iron (III) chloride solution was added to a 1-mL aliquot of the standard or sample. Duplicate analyses were run for each sample. The separation was carried out on a Hewlitt Packard 1090 HPLC equipped with an autosampler, a diode array UV/visible detector, and an Alltech Spherisorb ODS-2 5 µm 4.6 × 150 µm column. A flow rate of 1.5 mL/min was used with an injection volume of 100 µL. The Fe/chelate complex was detected at 254 nm. A calibration curve from the low microgram to the milligram level was run prior to sample analysis.

Appendix II.C:

Preliminary Germination Studies

Appendix II.C:

Preliminary Germination Studies

In the Miami-Erie Canal cleanup, a fundamental consideration must be the fitness of the treated soil for restoration to its original purpose. One important characteristic to maintain is that the washed soil must be able to sustain vegetative growth again, thus minimizing airborne dust and aesthetic damage. In order to obtain a first indication of how the treated soil would respond to a vegetation cover, and especially of how extensive a modification of the chemical composition of the treated soil would be necessary, preliminary phytotoxicity tests, based on germination-inhibition measurements, were run on a portion of treated uncontaminated Mound soil. The procedure adopted in this case, adapted from several methods used to assess the phytotoxicity of waste materials and substrates, utilizes watercress seeds as phytotoxicity indicators because of their high sensitivity to both organic and inorganic toxins and because of their fast, easy germination.

A first, baseline round of germination tests was conducted on samples of uncontaminated soil treated with the ACT*DE*CON^{SM} process. The treated soil was brought to saturation paste (the closest simulation of soil's interstitial solution composition) according to the *Methods of Soil Analysis, Part I,* (p.169, A.L. Page [editor], in the series *Agronomy*, American Society of Agronomy, Inc., Soil Science of America, Inc., Madison, Wisc., 1982), and then centrifuged at 3,000 rpm for 20 min. The supernatant was stored, and the solids were resaturated and centrifuged another time (wash samples 1 and 2). The supernatant from the second centrifugation was then acidified with 0.1 N sulfuric acid to pH 8.5, resaturated, and centrifuged twice (wash samples 3 and 4).

The four supernatant samples were analyzed for pH, electrical conductivity, and percent solids (see Table II.C.1) and tested for phytotoxicity according to the following watercress germination test. Twenty seeds of watercress (Frank Nurseries # 623 401397) were placed on Whatman #41 filters in a glass petri dish. The filters had been previously wetted with 2 mL of each wash sample, so that enough free liquid was present to wet the seeds without creating an

TABLE II.C.1 Analysis of the Four Supernatant Samples Used for the Germination Tests

Sample	% Solids	Electrical Conductivity (µS/cm)	pH
1	6.5	41,400	9.7
2	2.7	34,400	9.7
3	2.4	34,300	8.6
4	3.9	n/a	8.6

anoxic environment. Seeds were allowed to germinate at 20-22°C for 24 h, after which the percent germination was recorded. Each wash test was replicated three times and tested against a control of deionized water (DI). To evaluate germination, the following germination categories were established:

A. No change: seeds had not hydrated or germinated.

B. Swollen: seeds had hydrated but had not germinated.

C. No root growth: seeds had hydrated and teguments had cracked, but no root growth was visible.

D. Germinated: seeds had hydrated and root growth was evident.

E. Leaf growth: seeds showed presence of root and seedling.

The results from this preliminary round of testing showed no germination (all seeds were in category A) with any of the wash samples, compared with control trials showing at least 95% germination in 24 h.

A second series of trials was then performed, using the four wash solutions at two different dilutions (i.e., diluted 1:2 and 1:3). In this case, too, no germination was found, even in the most diluted samples (approx. solids concentration of 1%).

To evaluate whether the lack of germination was attributable to the inorganic components of the solution (mainly sodium bicarbonate), the same procedure was used to establish a baseline germination of cress seeds in pure sodium bicarbonate at 0.25, 0.50, 0.75, and 1% solution concentration. The germination test was then repeated on the first neutralized wash of the ACT*DE*CON^{SM}-treated soil (wash 3), brought to solids concentrations of 0.25 and 0.50%, and run against controls of 0 (deionized water), 0.25, and 0.50% sodium bicarbonate (the concentrations of bicarbonate that had previously given at least 40% germination). All solutions except the deionized water control had comparable pH values of approximately 8.5. Results (summarized in Table II.C.2 and II.C.3) show a definite decline of germination in pure bicarbonate at >0.5% and comparable germination between bicarbonate and wash only up to 0.25% concentrations. At 0.5%, the wash solution drastically inhibited the seeds' germination. Since this effect was not seen in the equivalent 0.5% bicarbonate solution, the hypothesis was formulated that the phytotoxic effect might be due to the bicarbonate and some other component(s).

The ACT*DE*CON^{SM} process drastically affects both the soil structure and the chemical composition. One potential cause of phytotoxicity is the presence of anaerobic decomposition

TABLE II.C.2 Germination Category Percentages in a Pure Sodium Bicarbonate Solution at Different Concentrations (results are mean values of three replications of 20 seeds each)

Bicarbonate Concentration	Category A	Category B	Category C	Category D	Category E
0 (control)	0	3.35	0	96.65	0
0.25%	1.70	0	6.65	91.65	0
0.50%	5.00	6.65	41.70	46.65	0
0.75%	10.00	5.00	80.00	5.00	0
1.00%	18.50	19.80	61.70	0	0

TABLE II.C.3 Germination Category Percentages in 0.25% and 0.50% Solids Neutralized Wash, Compared with Same Concentrations of Sodium Bicarbonate (data are mean values of three replications of 20 seeds each)

Sample	Category A	Category B	Category C	Category D	Category E
DI Water (control)	1.65	5.00	1.65	91.70	0
Bicarbonate 0.25%	1.65	3.33	5.00	90.00	0
Wash 0.25%	0	1.67	3.30	95.00	0
Bicarbonate 0.50%	5.00	1.65	45.00	48.30[a]	0
Wash 0.50%	8.30	11.65	76.65	3.40[a]	0

[a] Most of the 0.50% bicarbonate and wash test seeds in category D had evident signs of root damage (black root tip).

metabolites (such as sulphur compounds and volatile/short-chain organic acids) that could accumulate because the treated soil, being wet and with virtually no structure or pore space, can quickly turn anaerobic.

A final test was performed to evaluate whether the decrease in germination (Category D) found in the 0.5% wash sample vs. the 0.5% bicarbonate sample was due to easy-to-decompose/remove organic components. The 0.5% wash sample was, therefore, treated in three different ways to remove/degrade organic components and then retested for phytotoxicity, with a control of untreated wash and another of deionized water. The treatments were the following:

1. Air: air bubbling for 24 h; this treatment has been shown to decrease phytotoxicity in cases where it was due to volatile organic compounds.

2. H_2O_2: addition of 1 mL of 3% H_2O_2 to 20 mL of wash, to oxidize easily degradable organic compounds.

3. Carbon: addition of 1 g activated carbon to 20 mL wash, stirring for 20 min and then filtering through Whatman cellulose filter #42; this process was intended to physically remove the organic compounds in the wash, without removing the bicarbonate.

The results, summarized in Table II.C.4, show that none of these treatments significantly decreased the phytotoxicity of the original material, although a slight improvement was noticed with the activated-carbon filtration. It is possible, however, that similar but stronger treatment (e.g., an increase in the amount of hydrogen peroxide or a longer air bubbling) might prove effective.

Recommendations for Future Testing

It is evident from visual observation and from these preliminary results that the ACT*DE*CON^{SM}-treated soil, under the current treatment conditions, will require some significant further treatment if revegetation is desired. Preliminary data show that salinity or sodium bicarbonate might be responsible, at least in part, for the phytotoxic effect observed and that a better rinsing of the soil will be required.

A more in-depth evaluation of the soil-extractable toxins (both inorganic and organic) will be necessary, with more selective testing and analytical verification.

TABLE II.C.4 Germination Category Percentages in Washes at 0.5% Solids Concentration after Different Organics-Removal Attempts (mean values of three replications of 20 seeds each)

Sample	Category A	Category B	Category C	Category D	Category E
DIW control	1.65	3.35	5.00	90.00	0
Wash/control	6.65	33.30	43.35	16.65	0
Wash/air	0	18.35	81.65	0	0
Wash/H_2O_2	0	18.35	63.30	18.30	0
Wash/carbon	1.65	5.00	60.00	33.35	0

These tests necessarily will be completed by investigation of the physical aspects of the soil structure. These physical characteristics play an essential role in removing excess salinity and in maintaining healthy aerobic conditions, at least until the most unstable organic matter generated by the ACT*DE*CON^{SM} process has been either removed or microbially stabilized/mineralized.

Mound-ACT*DE*CON^{SM} Feasibility Study, Phase II: Final Report

Chapter III

Task 7 Waste Stabilization Study

by

John R. North
RUST Federal Services, Inc.

December 1994

Contents

Chapter III

Task 7 Waste Stabilization Study

by

John R. North
RUST Federal Services, Inc.

III.1 Work Description

Task 7 involved the study of stabilization methods for processing the secondary waste (residues) produced by the Mound soil ACT*DE*CON^{SM} and MAG*SEP^{SM} treatment processes. This work was to be performed at RUST's Clemson Technical Center.

Initially, the secondary waste was described as the regeneration solution used to remove recovered plutonium from the MAG*SEP^{SM} particles. In a full-scale program, it is reasonable to assume that the secondary waste stream will also include used or spent MAG*SEP^{SM} particles. Therefore, technologies identified for evaluation included cementation, evaporative drying, and vitrification. During the course of the test program, the anticipated secondary waste matrix changed to include only the MAG*SEP^{SM} particles, so evaporative drying technology was deleted from the test program.

III.2 Cementation

Stabilizing the secondary waste with cement compounds can be financially attractive when compared to vitrification. The equipment required for stabilizing the waste is simple and inexpensive.

A program was designed to test 12 different stabilizers, ranging from cement to a cement and lime mixture to a commercial mortar mix. These tests were to be conducted with waste loadings ranging from 50 to 80 weight percent. The resulting mixtures were to be evaluated by using quick leach procedures to establish performance trends. Tests with the most promising mixture was to be repeated to obtain sufficient quantities for conducting a complete chemical analysis for evaluating the technology.

III.3 Vitrification

In general, vitrification provides a waste product superior to that resulting from cementation technology. However, the equipment necessary for implementing vitrification is much more expensive to purchase and maintain.

When stabilizing MAG*SEP^{SM} particles, the organic constituent in the resin binder may cause the iron oxide in the particle core to separate from the melt. When the resin is oxidized to form carbon dioxide, the oxygen required for the reaction can cause the iron oxide to be reduced to iron metal. If the metal separates from the glass melt, the extractability of the contaminant is likely to be higher than anticipated for a monolithic glass melt.

The purpose of the test program was to maximize the waste loading without producing a metal phase. The phase diagram for the target glass formation is shown in Figure 3.4.2 of the project task plan (see Appendix III.A). The diagram is for a boro-silicate glass, which is considered to be a "low-temperature" forming glass (~ 1100° C). Three waste/glass-former mixes were to be tested. The test program was developed to examine if the particles themselves could be used to formulate the final glass product and, if so, to determine the maximum waste loading. The anticipated MAG*SEP^{SM} particle composition is 30 wt% magnetic core (iron oxide), 30 wt% zeolite material, and 40 wt% resin binder. The zeolite material contributes to the alumino-silicate material in the glass, while the magnetic core is used as part of the metal oxide glass. The waste loading probably cannot exceed 50 wt% without creating a separate iron metal phase.

III.4 Performance Criteria

The Nevada Test Site Waste Acceptance Criteria were chosen to be the performance standards for treating the MAG*SEP^{SM} particles. These criteria were chosen because the secondary waste produced from cleaning the Mound soil most likely will be considered a low-level TRU waste with an activity of less than 10 nCi/g. This assumption is reasonable since the Mound soil is contaminated in the pico-Curie range.

The Nevada Test Site Waste Acceptance Criteria are summarized below:

- No more than 1%, by weight, of the stabilized material is less than 10 microns in diameter.

- No more than 15%, by weight, of the stabilized material is less than 200 microns in diameter.

- The free moisture content of the stabilized material does not exceed 0.5% by volume.

- Chelating- or complexing-agent concentration is less than 1%, by weight, in the stabilized material.

- No listed/hazardous constituents are in excess of the allowed limits established by the EPA (40 CFR 261).

III.5 Task Plan

A project task plan was developed in August 1993, and it is appended to this task report as Appendix A. The conduct of the waste stabilization studies is governed by the task plan, which covers the task activities, procedures, health and safety issues, and other related issues.

Section 1.0 of the plan details the activities and control documents for the stabilization tests. These control documents include

- Task health and safety plan,
- Quality assurance plan,
- Sample and analysis plan,
- Decontamination and free release approval plan, and
- Waste disposal plan for the task materials and residuals.

Section 2.0 of the task plan enumerates the work activities necessary to characterize the secondary waste to use as a baseline for the treatability studies. The test work details for the cementation and vitrification technologies are listed in Section 3.0. The plan identifies the test variables to be examined for each technology.

III.6 Results

As discussed in other sections of this report, the MAG*SEP^{SM} test results were marginally acceptable, and the concept of using this technology to remove the extracted plutonium from ACT*DE*CON^{SM} solution has been suspended. Phase III will focus on optimizing the ACT*DE*CON^{SM} chemistry to remove the plutonium from the contaminated Mound soil and will not address the secondary waste treatment issue. This issue will be addressed after successful completion of Phase III, once the secondary waste matrix has been completely characterized.

Appendix III.A

Mound Phase II, Task 7, Task Plan, August 20, 1993

MOUND PHASE II, Task 7
Task Plan

(892032-04)

August 20, 1993

Review & Approvals

CTC Project Engineer:
Robt. S. Cooper ______ 8/23/93

CTC TD&D Lab Manager:
Dave E. McCartney ______ 8/30/93

CTC Health & Safety:
Dan Hogan ______ 9/1/93

RFS Proj. Mgr.:
Debbie Browning ______

Argonne Project Engineer:
Mike Wilkey ______

Argonne Project Manager:
Don Johnson ______

MOUND PHASE II, Task 7
Task Plan
August 20, 1993

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FORWARD

Provided here is the original description of this task.

TASK 7 - WASTE STABILIZATION STUDIES

Background and Basis for the Task

The regeneration solution will contain the recovered plutonium. This solution (and potentially the used magnetic separation particles) will require disposal as radioactive waste. This task will evaluate waste stabilization methods for processing the residues from the treatment process.

Work to be Performed

This task will characterize the waste material produced by the ACT*DE*CON^{SM} process, and perform studies of candidate treatment technologies. Technologies to be evaluated include cementation, evaporative drying of the residue, glassification and vitrification. This task will consider the availability and usefulness of existing treatment equipment at the Mound site, and the applicable DOE Waste Acceptance Criteria. This task will be performed in the Clemson Technical Center lab.

The subtasks to be performed include:

a. Characterize the waste product from the ACT*DE*CON^{SM} process to determine plutonium concentration, other solids concentration, pH, chelant, and any other parameters of interest.
b. Review with Mound site personnel the design and availability of any site equipment/facilities that may be of use in treating the waste product.
c. Evaluate waste characteristics and DOE Waste Acceptance Criteria against candidate technology requirements and performance to select the best potential candidate(s).
d. Perform lab-scale stabilization processing with candidate technology(ies).
e. Analyze product of lab-scale stabilization for compliance with the performance criteria in the DOE Waste Acceptance Criteria.

Purpose of the Task

To select, demonstrate and qualify the waste treatment method(s) to be utilized during the pilot and full-scale treatment operations.

Performance Goal

To demonstrate in the lab: 1) that the residues can be treated to meet required DOE standards; 2) that the residues can be treated at a cost of less than $30 per cubit foot of soil treated; and 3) that the waste product generated is less than 10% of the volume of soil treated.

Deliverables

a. Engineering Study Results
b. Waste Characterization Results
c. Non-proprietary Test Procedures
d. Test Results
e. Waste Billet Samples

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1.0 Preliminary Activities and Control Documents

The task specific activities which need to be addressed at the out-set are enumerated below with the individual(s) responsible for their completion.

1.1 Prepare Task Work Plan

After characterization, stabilization of the waste form is the goal of this task. Achieving this goal requires developing the necessary stabilization procedures, utilizing different stabilization technologies and evaluating stabilization mixtures. Achieving this goal quantitatively, involves measurement of specific waste acceptance criteria (WAC) parameters. The measured values of these parameters must be equal to or better than the requirements of the WAC for this project.

This task work plan identifies the task activities, the individuals responsible for those activities and the schedule for the completion of the activities. This task will be carried out by TD&D personnel at the CTC facility except for the vitrification activities. These are planned for execution at Clemson University's ESE Laboratories with TD&D personnel assisting.

The current list of project representatives for this task is as follows.

Primary Contact	Title	Alternate Contact	Title
Debbie Browning	RFS-Cola. PM	?	?
Neil Swift	Bradtec Scientist	Gede Kalinauskas	Bradtec VP Engrg.
Dave McCartney	TD&D Lab. Mgr.	Steve Hoeffner	TD&D Group Leader
Jesse Conner	Sr. Specialist	Jim Huffman	TD&D Group Leader
Steve Hoeffner	Group Leader	Tim Pruett	TD&D Group Leader
Jim Huffman	Group Leader	Tim Pruett	TD&D Group Leader
Lew Goodroad	Specialist	Bob Cooper	Project Mgr.
Bob Cooper	Project Mgr.	Al Meyer	Project Mgr.
Jim Resce	Clemson U. Sci.	Lew Goodroad	Specialist

The overall task schedule can be found in Appendix A, as Exhibit 1. The program covers approximately a 13 week period. For reference purposes, the original project schedule has also been included in Appendix A, as Exhibit 2. The original plan was to take the regeneration solution containing plutonium and small quantities of magnetic separation materials and stabilize it. We have been informed that the residual materials for stabilization will be exclusively the magnetic separation materials. Because of the quantity of soil and the concentration of the plutonium there will be sufficient material for stabilization. As a result, the plan for this task is now for CTC to use magnetic separation materials supplied by Bradtec, and spiked by CTC, for stabilization evaluation.

There are a number of issues as yet un-resolved which could significantly effect the schedule and dates indicated in this plan. These issues are associated with the availability/delivery of the materials, as well as, the constituents of the material and their chemistry. While the program has been modified for the above change in waste form, the program has included the magnetic materials which were actually used to treat the EG&G Mound soil. Elimination of this last actual material would simplify somewhat the task activities.

Resolution of these issues is imperative and should be obtained as soon as practical. without resolution the schedule will not be maintained.

The significant deliverables of this task are summarize~~s~~d below along with the individual that is responsible and the tentative due date for the deliverable.

No.	Deliverable Description	Responsibility of:	Due Date:
1	Issue Prel. Work Plan	Bob Cooper	Aug. 20, 1993
2	Mound/DOE WAC	Debbie Browning, (Col.)	Aug. 27, 1993
3	Initial Quantity of Soil	Neil Swift, Bradtec	Aug. 27, 1993
4	TPRAF for Task 6 Residuals	Neil Swift, Bradtec	Sep. 03, 1993
5	Waste Form(s)/ Mat. to CTC	Neil Swift, Bradtec	Sep. 03, 1993
6	Engineering Study	Conner-Huffman-Cooper	Sep. 10, 1993
7	Characterization Sum.	Conner-McCartney	Oct. 29, 1993
8	Test Procedures	McCartney-Hoeffner	Oct. 29, 1993
9	Test Results	Huffman-Hoeffner	Nov. 12, 1993
10	Send Sample Billets to ANL	McCartney-Cooper	Nov. 12, 1993

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During the execution of the Task 7 work there are a number of points within the schedule where **Holds** occur. Some are Project **Holds** allowing control of the project work to be with RFS. Others are technical in nature and are the responsibility of the CTC personnel. The Flow Diagramed Activities shown in Exhibit 3 of Appendix A illustrates the sub-task sequencing and inter-relationships. The **Hold** locations within the illustrated task work flow have been high-lighted for clarity.

Unless releases are obtained in a timely manner the schedule will not be maintained.

Hold Release by RFS	Sub-Tasks Authorized
A	1.1 ONLY (Verbal already received)
B	1.2 through 3.1
C	3.2 through 3.4
D	3.5 through 5.5

CTC Technical Holds	To Proceed Beyond Sub-Task:
1	3.1 (WAC Required)
2	3.4 (All 1.x Sub-Tasks Complete)
3	4.0 (All Bench Studies Complete)

1.2 Prepare Task Health and Safety Plan (HASP)

The CTC site Health, Safety & Environmental Compliance Program Plan issued February , 1993 will be the governing document for this task's activities. A task HASP will be written to identify task specific hazards, protective equipment, prescribed procedures and responsible personnel. It will also address the means of dealing with the identified hazards, precautionary measures, Special Personnel Protective Equipment (PPE), and additional training to prepare the personnel for addressing these hazards. The task HASP will be prepared by TD&D Project Personnel with review by the CTC Health and Safety Officer.

1.3 Prepare Task Quality Assurance Program Plan (QAPP)

The CTC Analytical Laboratory Quality Assurance Program manual (latest revision) as applicable shall be the governing document for this task's activities. A task QAPP will identify the task specific exceptions, additions and/or alternative procedures to be used in the maintenance of the task's quality assurance. The task QAPP will be prepared by TD&D Project Personnel with review by a TD&D Group Leaders.

1.4 Prepare Task Sample and Analysis Plan (SAP)

The latest revision of the standard site procedure (CTC 1045) will be the main governing document. A separate task SAP will identify the specific samples required, the means of obtaining those samples, the methods of analysis and supplemental instructions as needed, regarding duplicates and spikes. The task SAP will be developed by the TD&D Project Personnel and the TD&D Group Leaders with further review from the TD&D Laboratory Manager. **Table 1.4.1** enumerates the anticipated CTC Analytical Laboratory Procedures.

1.5 Prepare Task Decontamination and Free Release Approval Plan

The performance of this task's activities will expose both work space and equipment to hazardous materials. Since both the work space and the equipment are intended for re-use their condition after the conclusion of this task shall be determined. A document will be developed to provide the procedures to be used in reducing and/or eliminating the residual material or effects of this task's activities. The criteria to be used in deciding the issue of free release of equipment from CTC will be governed by this document (DAFRAP) as well as, the requirements of CTC's site permit and the applicable government regulation. The task plan will be developed by TD&D Project Personnel and the CTC Health and Safety Officer with review by the TD&D Laboratory Manager.

RRS - Clemson Technical Center Sample Analysis	Issued 08.20.93	Page 05/20
Mound Phase II, Task 7 **Table 1.4.1** - Anticipated Sample Analysis	Rev. No. (_/_/_)	

Based on the current task plan TD&D anticipates the following procedures will be required in the performance of this work.

Analytical Procedures for:

1. Initial Sample Receipt:
    - Fingerprinting
    - Physical Appearance
    - Radiation Screen
    - Ignitability
    - Corrosivity
    - Reactivity
    - Paint Filter Test
    - Toxicity, Full TCLP
    - Plutonium
2. Spiked MAG*SEP℠ Particle - Plutonium
3. Selected Cementation Stabilization Matrix Samples:
    - Physical Appearance
    - Radiation Screen
    - Ignitability
    - Corrosivity
    - Reactivity
    - Paint Filter Test
    - Toxicity, TCLP Metals Only
    - Plutonium
4. Vitreous Stabilization Matrix Samples:
    - Physical Appearance
    - Radiation Screen
    - Ignitability
    - Corrosivity
    - Reactivity
    - Paint Filter Test
    - Toxicity, TCLP Metals Only
    - Plutonium

1.6 Prepare Task Waste Disposal Plan (WDP)

The original waste disposal scenario had the materials from Bradtec, used to treat the Mound soil, being returned to Mound for disposal. That is, Mound in effect would receive the materials containing the contaminant originally obtained from their soil. With the complication of the additional materials and spiking at CTC the final disposition of the task residuals is subject to negotiation. From CTC's stand-point the simplest answer is for all the materials to be sent to Mound for disposal. The task WDP will address issues associated with additional packaging, labelling, handling and shipping of all task materials and residuals. It will be developed by TD&D Project Personnel and reviewed by the CTC Health and Safety Officer, the TD&D Lab. Manager and the Analytical Lab. Manager. Without resolution of waste disposal the program will not be started.

1.7 Perform Literature Review

A reference list will be provided enumerating the sources used in the execution of this task. The list will have three main categories: (1) Characterization, (2) Cementation Stabilization and (3) Vitrification Stabilization. TD&D Project personnel will be responsible for compiling these information sources.

1.8 Stabilization Criteria

The chemical and/or physical criteria establishing the basis for the successful stabilization of the materials should be by the customer's Waste Acceptance Criteria (WAC). Along with the acceptance criteria, the type of analysis, location performing the analysis, detection limits for the procedures, analytical accuracy and quantity of determination for the level of confidence needed. CTC has been directed to use the Nevada Test Site (NTS) Waste Acceptance Criteria in the absence of EG&G Mound Site WAC. Table 1.8.1 summarizes the criteria to be used by TD&D personnel in evaluating the stabilized materials an applied technologies. RFS-Columbia Project Management is to provide confirmation of these criteria or copies of the applicable Mound/DOE WAC, which indicate such other criteria as are to be used in CTC's evaluations.

1.9 Economic Issues

The criteria of the client are the volume reduction achieved through stabilization and the cost per unit volume of soil treated. A ten to 1 volume reduction and a $30. per cubic foot of soil treated have been established as the criteria against which stabilized technologies' performances will be judged. Bradtec will be responsible for providing CTC with the initial quantity (mass and volume) of soil materials treated. CTC Project Personnel will calculate the volume reduction and estimate the cost per cubic foot of soil treated.

RRS - Clemson Technical Center ANL - EG&G Mound Site	Issued 08.20.93	Page 07/20
Mound Phase II, Task 7 TABLE 1.8.1 - Waste Acceptance Criteria	Rev. No. (_/_/_)	

Stabilized Material Meeting These Requirements Shall Be Deemed Acceptable.

Parameters	Criteria	Stipulated in	Methods of Analysis
○ Corrosivity	pH >2. &<12.5	40 CFR 261.22	EPA Method 9045, ASTM D-4980.89
○ Reactivity	Non-reactive	40 CFR 261.21	CTC Standard Fingerprint testing. (H_2O, Sulfides and Cyanides)
○ Ignitibility	Doesn't Ignite	40 CFR 261.21	CTC Standard Fingerprint testing and requirements of 49 CFR 173.151
○ Free Liquid	Free Liq. < 0.5%	NTS WAC Req't.	CTC 1002 Wt % Free Liquid with CTC 92-69 Wt % Moist.
○ Particle Size	1 % max. < 10 μ 15 % max. < 200 μ	NTS WAC Req't.	Sieve Tray Analysis
○ EDTA	1 % maximum	NTS WAC Req't.	ASTM D-3113-87
○ Radioactivity	< 100 nCi/gram	NTS WAC Req't.	Radiation Screen

2.0 Receive and Characterize the Process Residuals

As indicated earlier from discussions with Bradtec, the process residuals will be the magnetic separation particles from the Task 6 regeneration work and will contain plutonium. After the completion of the Task 6 work at Bradtec - UK, they will send these materials to CTC for use in the Task 7 Stabilization Studies. Bradtec has subsequently indicated that the quantity of materials from their regeneration work will not be sufficient for all the stabilization efforts. Their recommendation has been to take un-used materials and spike them for use in the stabilization evaluations. This plan has been written under the assumption that both materials will be received by CTC.

2.1 Receive MAG*SEP℠ Particles

Since the task's program is to use the materials generated elsewhere, a TPRAF will need to be completed by Bradtec. This will be sent to Bradtec - Atlanta for completion either there or at their UK facilities. The authorization number for this material must be in place prior to its shipment to CTC. Once received, the materials will be logged into the CTC inventory for tracking and management. (See Appendix B for CTC TPRAF Document.) Bradtec is also responsible for providing information on the initial quantity of soil used in the Task 6 work.

2.2 Fingerprint materials Received

In addition to the Standard CTC Total Fingerprint, CTC plans to have the following performed or reported: (1) Physical Appearance, (2) Radiation Screen, (3) Ignitability, (4) Corrosivity, (5) Reactivity, (6) Paint Filter Test, (7) Full TCLP, and (8) Iso. Plutonium for the materials resulting from the Task 6 program. The necessary Sample Analysis Request Forms (SARF's) will be generated by TD&D Project Personnel. (See Appendix B for "SARF")

2.3 Evaluate the Quantity of Materials Received

CTC will confirm that the materials received either will or will not be sufficient to meet the requirements for processing with the selected stabilization technologies. The amount of material required for the stabilization investigation has been estimated at approximately 1950. grams (See Appendix C).

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2.4 Characterization of Received Materials

The testing performed in addition to the fingerprinting (para. 2.2) above will, provide the information necessary to characterize the materials received and to evaluate the suitability of the stabilization technologies.

2.5 Prepare "Artificial" Supplemental Material if Needed

If necessary, based on the previous evaluation (para. 2.3), the procedures will first be written and then the additional materials will be prepared to simulate the spent MAG*SEP^{SM} Particles. Bradtec will provide their recommendations regarding the appropriate spiking procedures. Bradtec will also provide the required MAG*SEP^{SM} Particles. TD&D Project Personnel will write the site procedures and perform the required spiking of the materials provided by Bradtec.

2.6 Characterization of Supplemental Materials

The supplemental materials will be characterized as to plutonium content for comparison with the materials from the regeneration work of Task 6. Since the materials are to be the same as those used in Task 6 no additional test is anticipated. The Sample Analysis Request Forms (SARF's) will again be generated by TD&D Project Personnel.

2.7 Characterization Summary

Both the original and supplemental material's characteristics will be enumerated and compared. This summary will be written by TD&D Project Personnel.

3.0 Stabilization of Materials

The candidate technologies for the planned stabilization of the residual materials are evaporative drying followed by either cementation or vitrification. The best technology will be determined by comparison of the stabilized materials analysis with the DOE WAC. As a result of the planned stabilization of un-used MAG*SEP^{SM} Particles the need for evaporative drying may be reduced.

3.1 Review Mound Equipment Available

Existing equipment at the EG&G Mound site may prove useful in processing the materials during the field programs. Consequently, the TD&D Project Engineer will review the existing site equipment from the stand point of using it in one or more of the stabilization processes. At this point, equipment of interest would be conveyors, grizzly scalping, screening, metering and mixing equipment along with tankage and slurry pumps. To expedite the review process the Mound site will be requested to supply a list of potential equipment currently or anticipated to be available for use in the field programs. A critical issue to the safe and appropriate utilization of the site equipment will be the availability of equipment documentation. In an effort to provide the site a check-list summary of typical documentation, **Table 3.1.1** will be sent.

3.2 Review DOE Waste Acceptance Criteria

The applicable DOE (Mound) WAC is to be specified by Argonne National Laboratory. In the absence of the specific Mound WAC, RRS - Columbia has directed the use of the Nevada Test Site (NTS) WAC. The NTS WAC has been used to identify the following criteria for evaluating the stabilized materials:

- Corrosivity, Reactivity & Ignitibility
- Free Liquid
- Particle Size Distribution
- EDTA
- Radioactivity

Table 1.8.1 previously identified these criteria, their limits and the methods applicable to the determination of the parameters. If an alternate WAC is subsequently specified, it will need to be reviewed for its impact on this Task's activities. An alternate WAC at this juncture will result in the schedule not being maintained.

3.1.1 EQUIPMENT DOCUMENTATION SUMMARY EG&G Mound Site (Miamisburg, Ohio)	Issue: Preliminary Date: 08.20.93	Equip.:	Table 3.1.1 (Page 11/20) Equipment Documentation

The manufacturer should have submitted drawings, documentation and data indicated and in the media and formats (print, disk, etc.) specified.			PROPOSALS REQUIRE	CONTRACTS REQUIRE	Proj. End REQUIRES
0.01 Assembly/Arrangement Drawings (w/ empty & oper'g. weights)					
0.02 Component Detail Drawings (with weights)					
0.03 Bills of Material (Manufacturer Name, Address & Phone No.'s)					
0.04 Piping and Instrumentation Drawings					
0.05 Electrical Schematic Drawings (__), (DCS I/O List (__))					
0.06 Wiring Diagrams (__), (Single Line Diagram (__))					
0.07 Motor Data and Drawings					
0.08 Equipment List (Loadings for Supports/Foundation Design(__))					
0.09 Support Steel, Foundation and Mounting Bolt Plan Drawings					
0.10 Allowable Nozzle Loads and Thermal Movements (Calc's.(__))					
0.11 Valve List (and Control Valve Sizing/Specifications (__))					
0.12 Specialty Piping Item List (and Vendor Catalog "Cuts" (__))					
0.13 Instrument List (and Individual Specification Sheets (__))					
0.14 Performance Curves/Data (Performance Test Report (__))					
0.15 Test Data/Curves (Instrument Calibration Sheets (__))					
0.16 As-Built Drawings and Data Forms					
0.17 Control Philosophy					
0.18 System Operating and Maintenance Instruction Manuals					
0.19 Component Service and Maintenance Instruction Manuals					
0.20 Erection Drawings and/or Installation Instructions					
0.21 Schedule (with Staffing Requirements Indicated (__))					

Drawing Revision

No.	Date	Description

Notes: 1. Minimum Drawing Size is 11" x 17" ("B" Size) with minimum 0.5" Borders. Each Drawing shall have a Title Block, Review-Approval Area and a Note Area. All Drawings shall identify the Vendor, the Equipment/System Name and Number, and the Project Name and Reference Number(s). Scale shall be indicated as appropriate.
2. Abbreviations: M1, "Blue-line" print; M2, Milar Reproducible; M3, "Sepia" original; M4, "Electronic" (Diskette); "C", Certified (for Construction); S1, Professional Engineer Sealed; S2, Structural Engineer Sealed; S3, Architect Sealed Drawings.
Ref:893-081.30

DOCUMENTATION SPECIFICATION

	By	Date
Dr	R.S.Cooper	08-20-93
Ck		
Ap		

3.3 Review Candidate Treatment Technologies

As part of evaluating the suitability of the planned technologies for stabilization of the materials in question, TD&D will review past applications of the technology and provide typical performance information. This will provide another means of comparing this program's results for the stabilization parameters.

3.4 Prepare Procedures for the Planned Technologies

3.4.1 For the cementation technology, **Table 3.4.1** summarizes the program matrix of stabilization mixtures. Briefly, the matrix mixtures will be prepared and evaluated using quick leach procedures to establish trends and relative performances of the mixtures. The most promising mixtures will be prepared again in sufficient quantity to allow preparation of three (100 gram minimum) billets of the stabilized material. One billet will be subjected to the complete analytical program previously identified in Table 1.4.1, under item 2, as well as, a pocket penetrometer measurement of the material's 7 day strength. One billet will be held for data corroboration if necessary. The third billet will be sent to Argonne National Laboratory for their use. The procedures for this stabilization evaluation will be prepared by the TD&D Group Leaders, with review by the TD&D Lab Manager and Project Engineer.

3.4.2 For the Vitrification technology, **Table 3.4.2** summarizes the program matrix of stabilization mixtures. Generally speaking vitrification should provide better stabilization results than the cementation technology. This results from the much lower solubilities of the glass material. In this particular instance, we can not be certain that this will occur. The MAG*SEP^{sm} Particles have a major organic constituent in the resin bonding the materials together. During vitrification at elevated temperatures this organic material will oxidize to both carbon dioxide and carbon monoxide particles. One likely source of the needed oxygen would be the iron compounds of the magnetic core. If oxygen scavenging by the organics from the iron occurs in too great an amount the iron contents will be reduced to iron metal and separate from the glass materials. The extractability of the metals and contaminants probably contained in the separated iron, is likely to be substantially higher than typically anticipated for glass alone.

As indicated in **Figure 3.4.2**, we have selected a target glass composition and will pursue its formation with three separate contribution levels of MAG*SEP^{sm} Particles. That is, a portion of the silicon-aluminum oxide materials are anticipated to come from the zeolites contained in the MAG*SEP^{sm} Particles. This evaluation should indicate just how equivalent a contributor the particles are and to what extent the organics interfere with the vitrification process. As indicated in the phase diagram of **Figure 3.4.2**, the glass to be formed will be a boro-silicate glass. While these generally fall into a category of low temperature glasses, the temperature required (1100 •C.) still exceeds the capabilities of the equipment at CTC.. Accordingly, CTC has made arrangements with Clemson University to conduct the vitrification portion of the stabilization work. Clemson personnel will be responsible for preparing the procedures necessary for the vitrification efforts. TD&D project personnel will have the opportunity to review and comment on the Clemson procedures. The vitrification will be carried out by Clemson University personnel with CTC-TD&D personnel assisting and witnessing the work there.

If Clemson University ESE Lab. does not have a license for radioactive materials (specifically for Plutonium) the MAG*SEP^{SM} particles with either be spiked with a plutonium surrogate (Cerium) or they will be left un-spiked altogether. The last case would only demonstrate the feasibility of the vitrification process and would not generate stability information. The currently planned plutonium surrogate, cerium; however, because it has radioactive isotopes may also need to be approved by the CTC and ESE Radiation Safety Officers. Spiking with cerium, if it is to be carried out, may need to be done by ESE. [Under review.]

3.4.3 "Block" type flow diagrams will be developed by TD&D project personnel to identify the steps of the stabilization procedures used in this program. Reagents needed for the stabilization(s) will also be determined and obtained by the personnel conducting the stabilization activities.

3.5 Process Equipment for the Planned Technologies

The bench scale stabilization equipment shall be set up and reviewed by the TD&D project team, including CTC's Health and Safety Officer, prior to the commencement of stabilization.

3.6 Stabilize the Material(s) using the Planned Technologies

The cementation and vitrification stabilizations will be carried out con-currently at CTC and ESE respectively. Adjustment in the stabilization proportions and mixtures will be made as appropriate, based on the results of the program as it proceeds. The ultimate goal is to generate solid billets of stabilized residuals for comparison with the DOE WAC requirements enumerated above. A billet representing each of the stabilization(s) demonstrated, shall be held for inspection by, later transfer to and finally analysis by Argonne National Laboratory.

3.7 Analyze the Stabilized Material(s)

Billets of stabilized materials are to be prepared for testing to evaluate the material against the WAC requirements:

- Corrosivity, Reactivity & Ignitibility
- Free Liquids
- Particle Size Distribution
- EDTA Content
- Radioactivity
- TCLP Metals
- Plutonium

Preparation for analysis includes size reducing the billets to meet the requirements of the TCLP protocol which has an upper particle size limit of 3/8 inch.

3.8 Send Sample Billets to ANL

Representative samples of the billet(s) generated will be sent to ANL as soon as practical after the completion of the each demonstration. Analysis of stabilized material billets at CTC will be used to complete the paper-work needed to ship the billets to ANL.

	RRS - Clemson Technical Center	Issued	Page
	<u>**Stabilization Matrix**</u>	08.20.93	15/20
	Mound Phase II, Task 7 Table 3.4.1 - Cementation Technology Matrix	Rev. No. (_/_/_)	

Anticipated Waste Form: MAG*SEP^{SM} Particles spiked with Plutonium to the level specified by Bradtec. (**)

Matrix	Stabilizer Proportions for Mix 1	Mix 2	Mix 3	Mix 4	MAG*SEP^{SM} Proportion
1. Cement Only (*1)	0.25	0.50	0.75	1.00	1.00
2. Cement & Lime (*1 & *2)					
Cement Proportion	0.5	0.5	0.5	0.5	
&					1.00
Lime Proportion	0.1	0.2	0.3	0.4	
3. Commercial Mortar Mix	0.25	0.50	0.75	1.00	1.00

** If sufficient MAG*SEP^{SM} particles are received from the actual Mound Soil work of Task 6, the material will be mixed in the most promising proportions for cementation stabilization and analyzed for comparison with the spiked materials performance.

*1 ASTM Type I, CSA Normal (Commercial Grade) (0.5 # H2O per # Cement)

*2 High Calcium Quick Lime (< 5 % Magnesium Oxide Content)

*3 Commercial Mix specifications and composition to be obtained from Manufacturer.

RRS - Clemson Technical Center **Stabilization Matrix**	Issued 08.20.93	Page 16/20
Mound Phase II, Task 7 Vitrification Technology	Rev. No. (_/_/_)	

Anticipated Waste Form: MAG*SEP^{sx} Particles, spiked as acceptable with Clemson University's ESE laboratory. The anticipated composition of the particles is: 30% Magnetite core (Mag.), 30% zeolite material (Zeo.) and 40% resin binder (Res.).

Mixture		Proportions MAG*SEP^{sx} Materials Mag.	Res.	Zeo.	Proportion SiO2+Al2O3 added mat'l.	Proportion B2O3 Eqv.	Proportion R2O
1	(25%)	0.33	0.44	0.33	1.00	0.67	0.67
				-------50 %---------		25 %	25 %
2	(40%)	0.67	0.89	0.67	1.00	0.835	0.835
				-------50 %---------		25 %	25 %
3	(50%)	1.00	1.33	1.00	1.00	1.00	1.00
				-------50 %---------		25 %	25 %

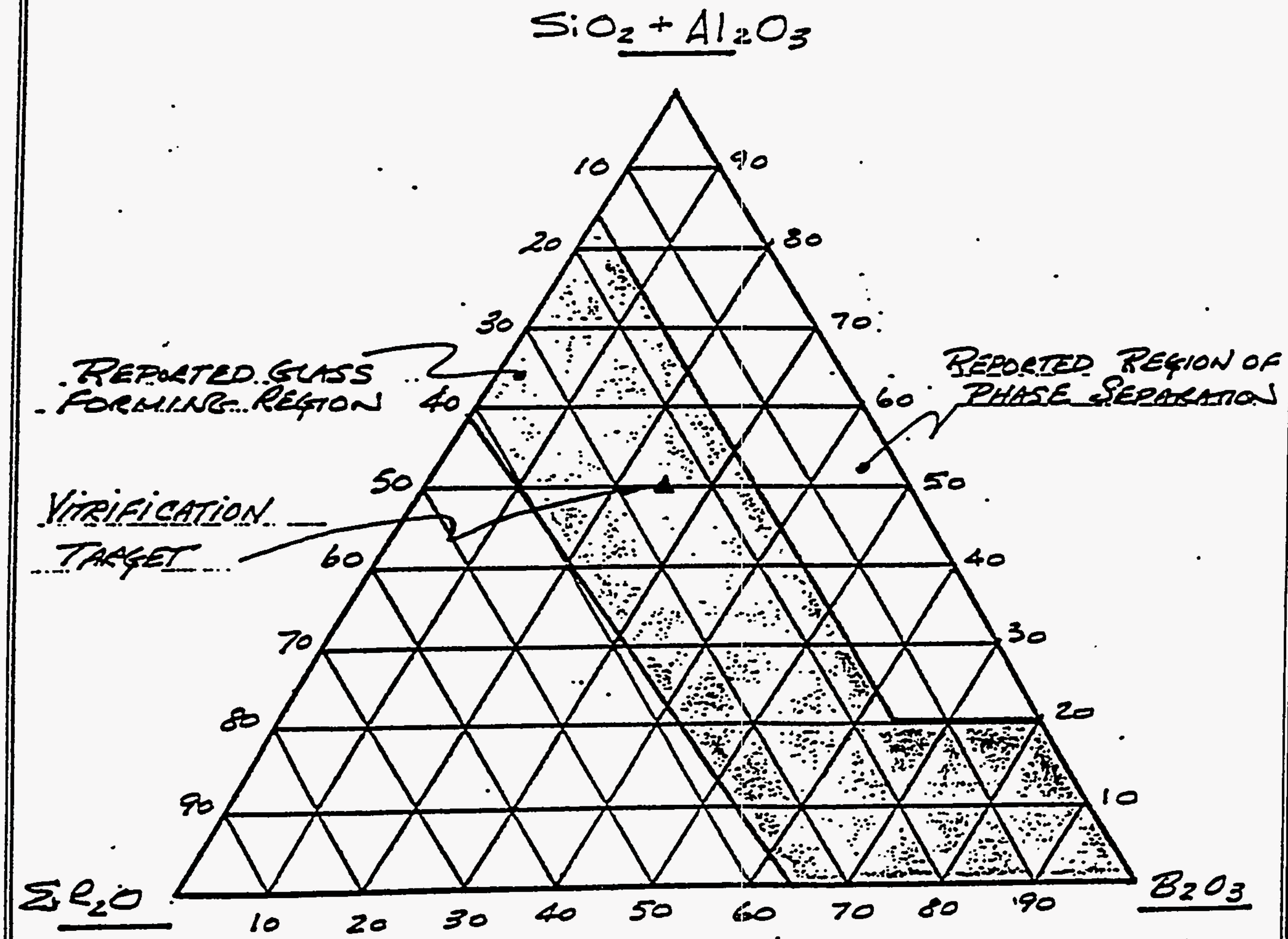
As shown above, the proportion of zeolites in the mix increases from mixtures 1 through 3. That is, the zeolite in the MAG*SEP^{sx} Particles is to provide a progressively larger proportion of the alumino-silicate material needed to form the glass. Con-currently the magnetite will have to be utilized as a correspondingly larger portion of the "R2O's" for the glass mixture. In mixture 3 the iron has to provide all of the R2O's required for the glass. Beyond mixture 3 the iron would likely form a separate phase from the glass phase.

The percentage shown after the mixture number corresponds to the amount of the alumino-silicate compound contributed by the MAG*SEP^{sx} Particles.

In each case the mixture is to have a final composition approaching the target values identified in Figure 3.4.2 (50:25:25).

	RRS - Clemson Technical Center	Issued	Page
	Calculations & Documentation	08.20.93	17/20
	Mound Phase II, Task 7 **Figure 3.4.2 - Boro-Silicate Glass Phase Diagram**	Rev. No. (_/_/_)	

Target Glass Formulation is 50 % $SiO_2+Al_2O_3$, 25 % B_2O_3 Eqv. and 25 % R_2O. The "R" represent alkali, alkali earth and metal oxides of the appropriate valence.



4.0 Waste Disposal

As a part of this task's efforts, disposal will be required for unused materials, generated materials, analytical residuals, and contact materials.

4.1 Process Residuals Plan and Preparation

CTC and ESE will endeavor to minimize the amount of excess starting materials. Both laboratories will maximize the use of the Bradtec-UK supplied materials and minimize the amounts of prepared materials needed for the technology(ies) to be demonstrated. There may be excess starting materials which will have to be disposed. Likewise the stabilized materials will exceed the amounts needed for analysis. Disposal of these excesses will also be required. The current plan calls for these materials to be placed into containers and sent to the Mound site for disposal. The task waste disposal plan will govern the disposition of the materials from this task. All of the materials used in this program are planned to be sent to the Mound Site for ultimate disposal by Mound.

4.2 Analysis Residuals Preparation

From initial fingerprinting to final TCLP testing, the materials remaining at the conclusion of the task analytical work will be placed in containers for shipment to the Mound site for final disposal. TD&D Technicians will be responsible for packing the residuals for shipment to the Mound Site for disposal by Mound.

4.3 Contact Wastes Preparation

Items coming in contact with the materials in this program or used in the restricted zone (except those items which can be decontaminated) will be placed in containers after their use and managed prior to being shipped to the Mound site for final disposal. It will be the responsibility of all those persons entering the controlled zone to place their contact materials (such as PPE) into the designated container.

4.4 Packaging and Shipment

Items for disposal will be placed in containers, appropriately identified, managed for duration of stay at CTC, shipped with the required documentation to Mound for final disposal. TD&D Technicians will be responsible for performing these operations.

4.5 De-contaminate Equipment

Equipment owned by CTC will either be de-contaminated for re-use or cleaned and packaged for restricted access storage. Rental equipment shall be decontaminated for return or purchased out-right and packaged for restricted access storage. These operations are to be carried out by TD&D Technicians with the supervision and review of the project engineer and the Radiation Safety Officer.

4.6 De-contaminate Site/Area

The area where the demonstration(s) are carried out is to be decontaminated to the level(s) approved by the Site Radiation Safety Officer.

4.7 Status - Summary

As a part of this task, a Status/Summary report will be generated covering the status of each container of material being managed and a summary of the findings regarding the decontamination of the task equipment and work area.

5.0 Final Report

The final report will contain all of the client required deliverables except the waste billet samples which will be sent separately to ANL. The TD&D Project Engineer will be responsible for assembling this report.

5.1 Engineering Study Results

This portion of the report reviews the Mound site equipment available and the candidate technology(ies) most likely to make use of the equipment.

5.2 Waste Characterization Results

The portion of the report summarizes the characterization of the materials received from Bradtec and, based on past similar application the best candidate technology(ies) to apply to achieve the requirements of the DOE WAC.

5.3 Non-Proprietary Test Procedures

This section presents the procedures used to stabilize the materials received from Bradtec, excluding those processing details of a proprietary nature. Both planned stabilization technologies will be addressed.

5.4 Test Results

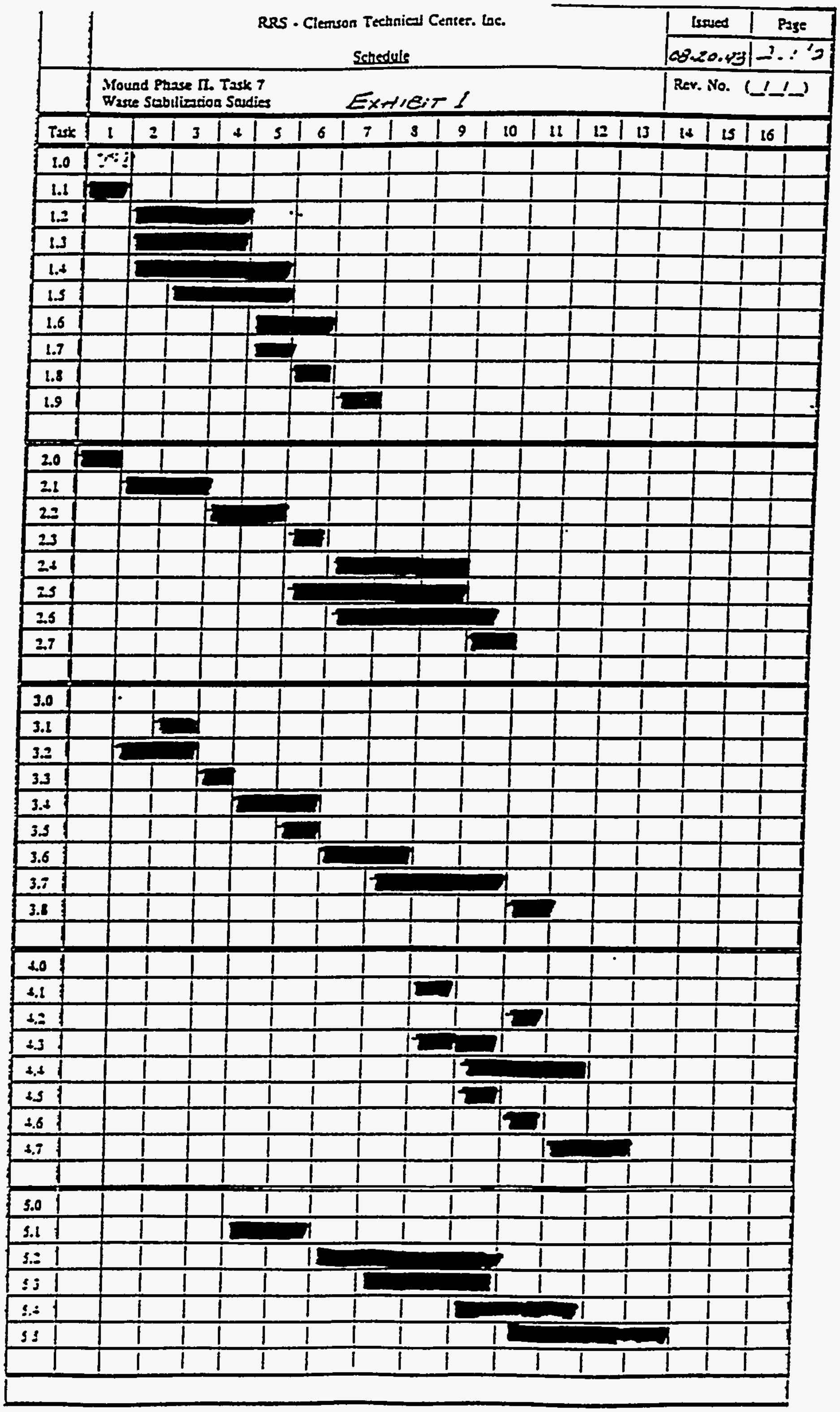
The final section presents the results of the analysis of the waste billets versus the requirements of the DOE WAC for both planned stabilization technologies.

5.5 Close-Out Report

The summary of the task costs and expenditures is to be generated for internal review and comment. The close-out report should also include summaries of problems encountered, solutions found and recommendations for either future investigations or similar demonstrations. The close-out report is the responsibility of the TD&D Project Manager and the CTC Accounting Manager.

RRS - Clemson Technical Center

APPENDIX A



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Schedule

Issued 08.20.93

Page 2 . : '3

Mound Phase II, Task 7
Waste Stabilization Studies

EXHIBIT 1

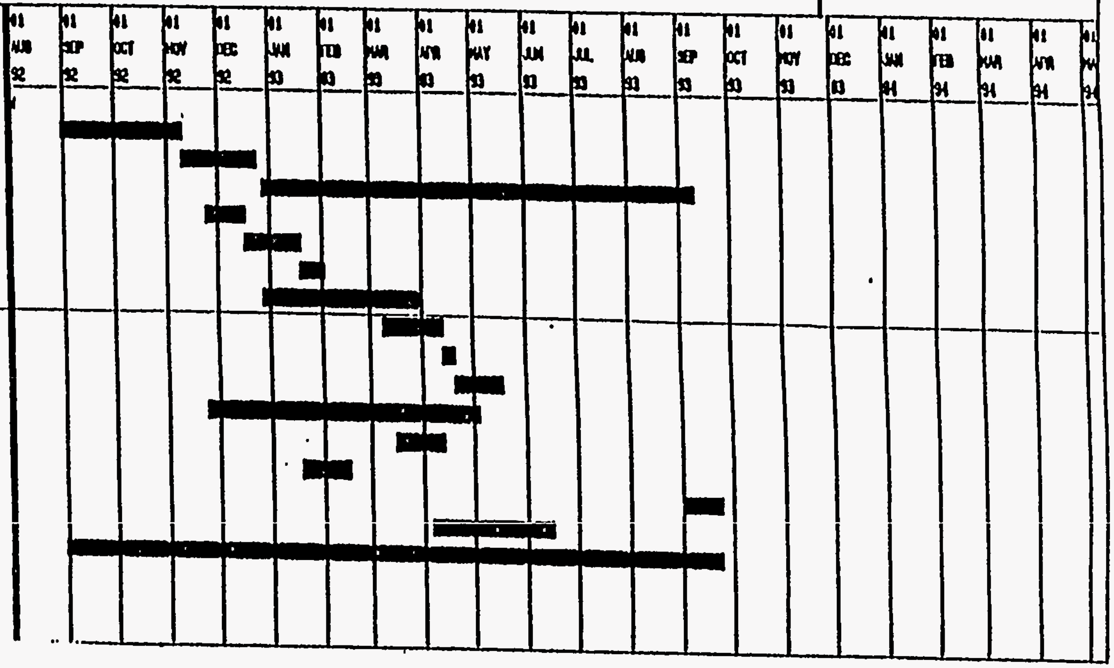
Rev. No. (/ /)

EXHIBIT 2

OPEN PLAN (R)
Report:
Project:
Time Now:
Date:
Time:
Panel: A

Ph II MOUND SOIL TREAT - Lab Scale Proof

Activity	Description	Start	Finish	Dur
0100	OPTIMIZE DISSOLUTION CHEMISTRY	31AUG92	09NOV92	50
0350	EVL DISSOLUTION OF NON HAZ MTL	10NOV92	23DEC92	30
0300	[illegible] STUDIES	26DEC92	08SEP93	180
0400	ION EXCHANGE MATERIAL STUDIES	24NOV92	15DEC92	15
0500	MAG PART OPTIMIZATION STUDIES	17DEC92	14JAN93	20
0600	MAG PART REGENERATION STUDIES	15JAN93	01FEB93	10
0700	WASTE STABILIZATION STUDIES	28DEC92	29MAR93	65
0800	LAB SCALE INTEGRATED TEST	09MAR93	12APR93	25
0900	L/S TEST W/MOUND SITE ACT SOIL	13APR93	19APR93	5
1000	INTEG TEST W/ACTIVE MOUND SOIL	20APR93	17MAY93	20
1100	HYDROGEOLOGICAL STUDIES	24NOV92	03JUN93	130
1200	HYDROGEOLOGICAL TESTING	15MAR93	12APR93	20
1300	CONT SOL MAG PART RECOVERY TST	15JAN93	15FEB93	20
1400	PREPARE FINAL REPORT	02SEP93	23SEP93	15
1450	PREPARE PATL DOCUMNT REPORTS	06APR93	15JUN93	50
1500	PROJECT MANAGEMENT	31AUG92	23SEP93	270



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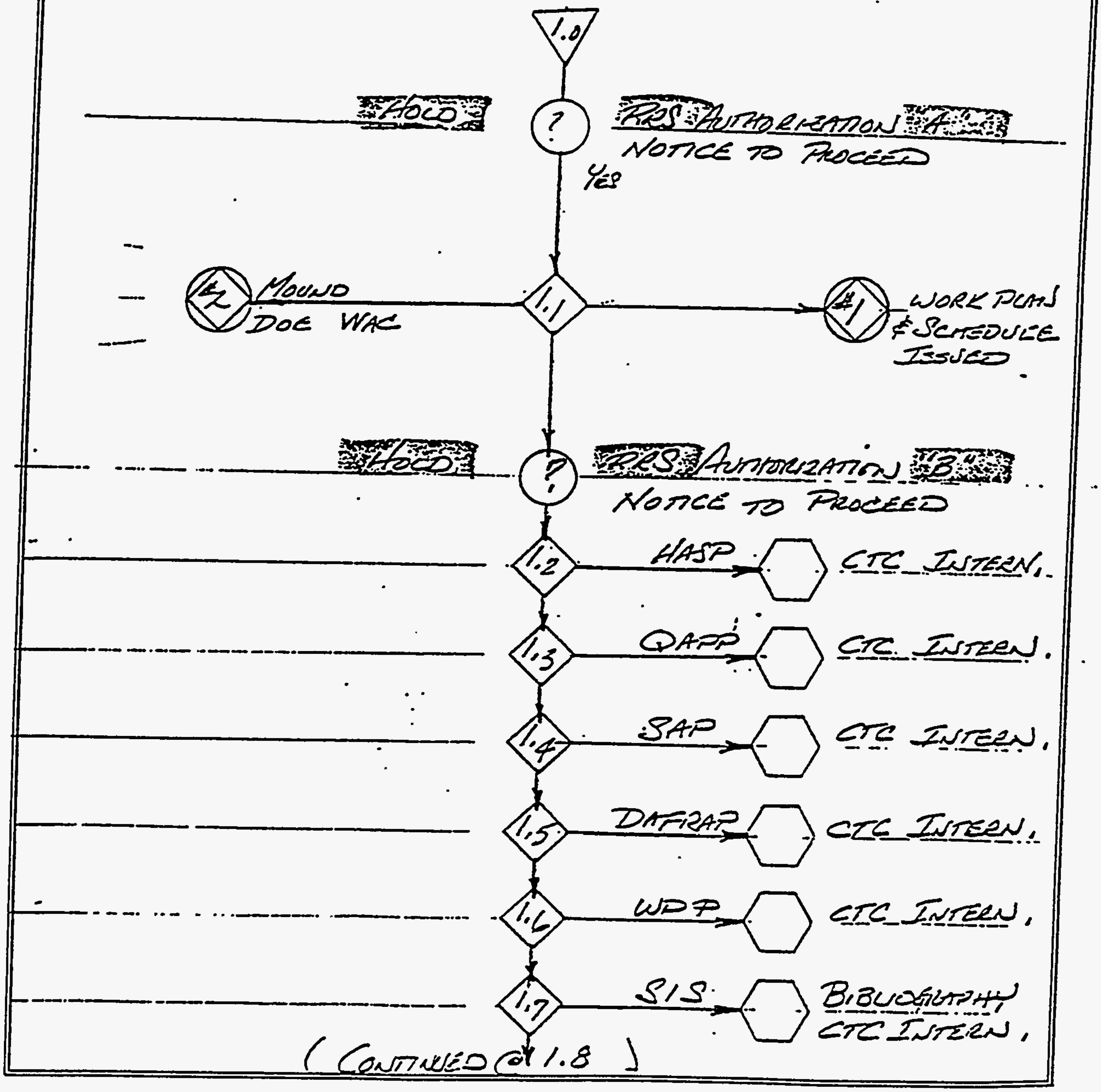

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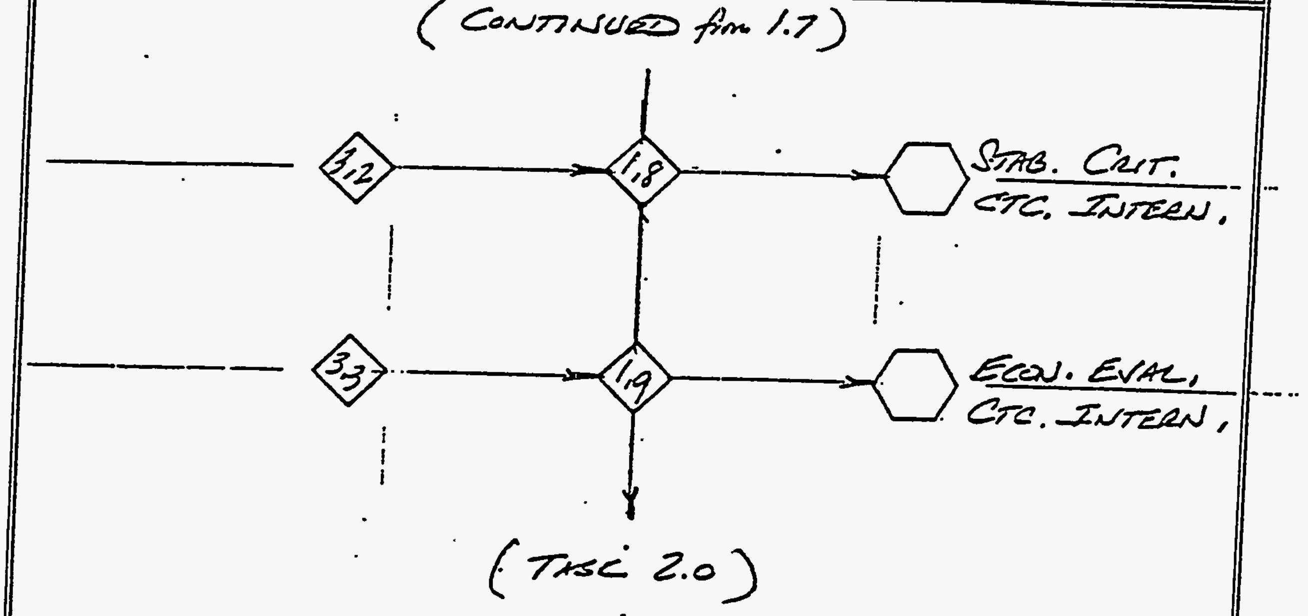
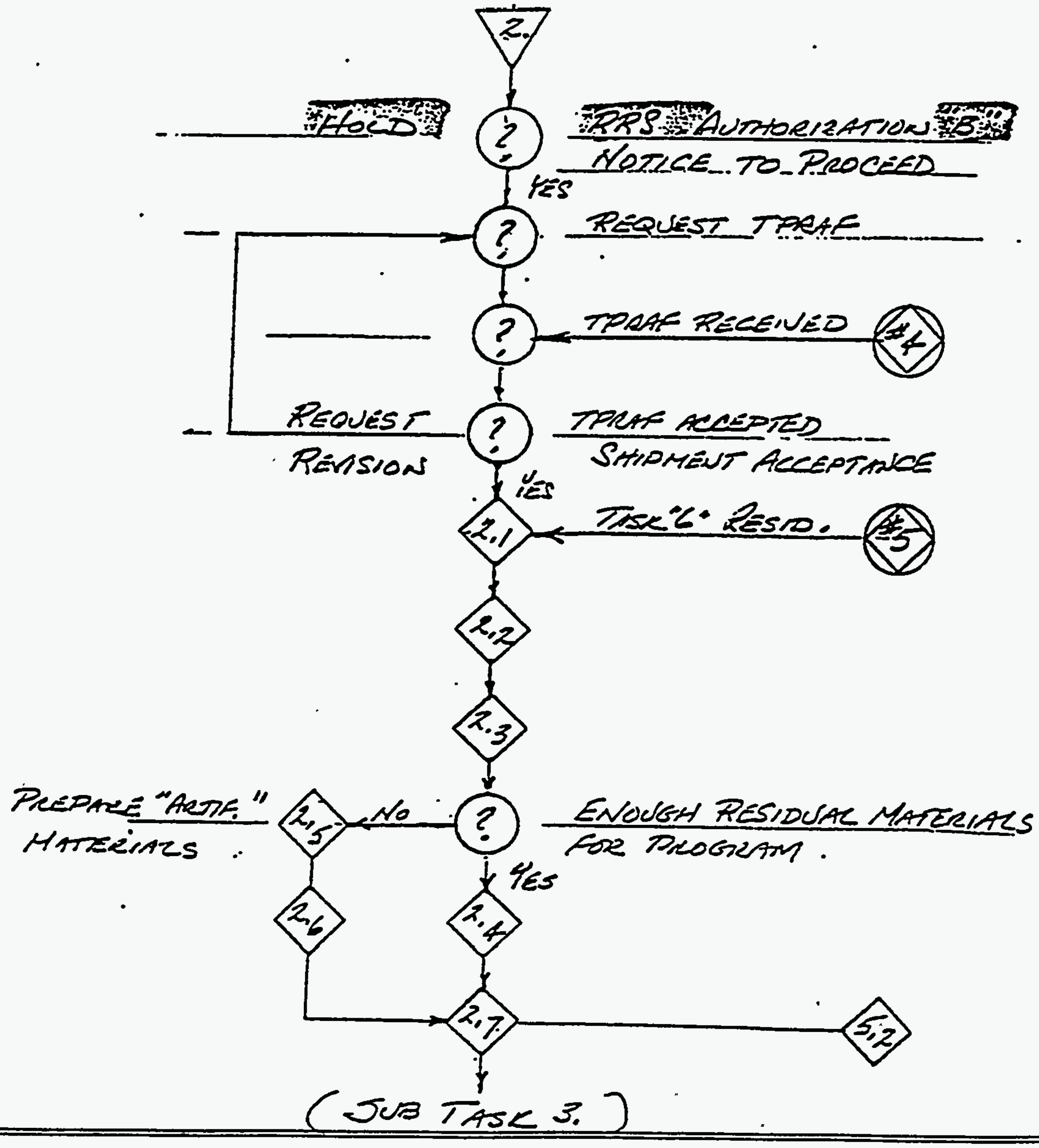


RRS - Clemson Technical Center, Inc. **Schedule Development**	Issued	Page 4-5/9
Mound Phase II, Task 7 Waste Stabilization Studies	Rev. No.	(1 1)



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RRS - Clemson Technical Center, Inc. **Schedule Development**	Issued	Page A-6/9
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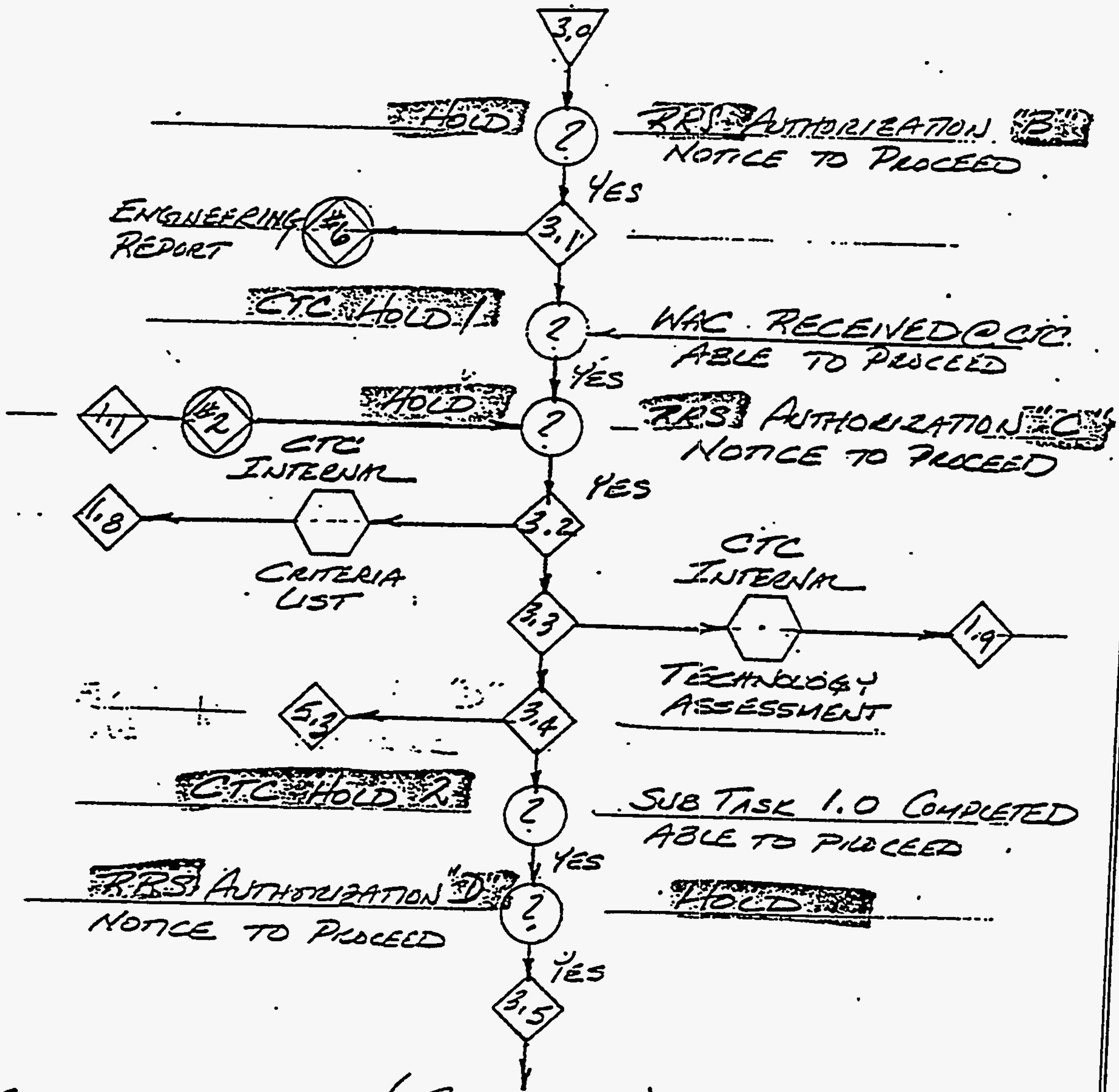

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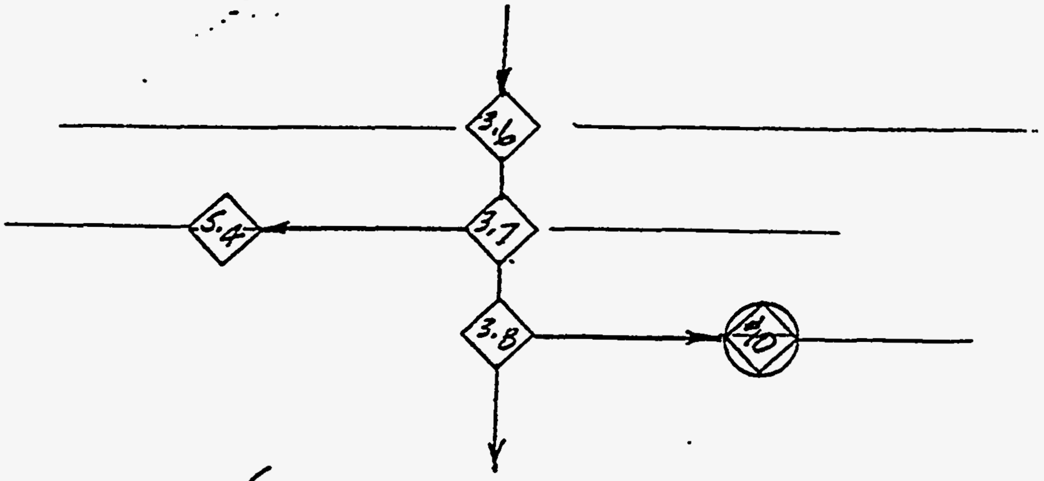
(CONTINUED FROM 3.5)



(SUB-TASK 4.)

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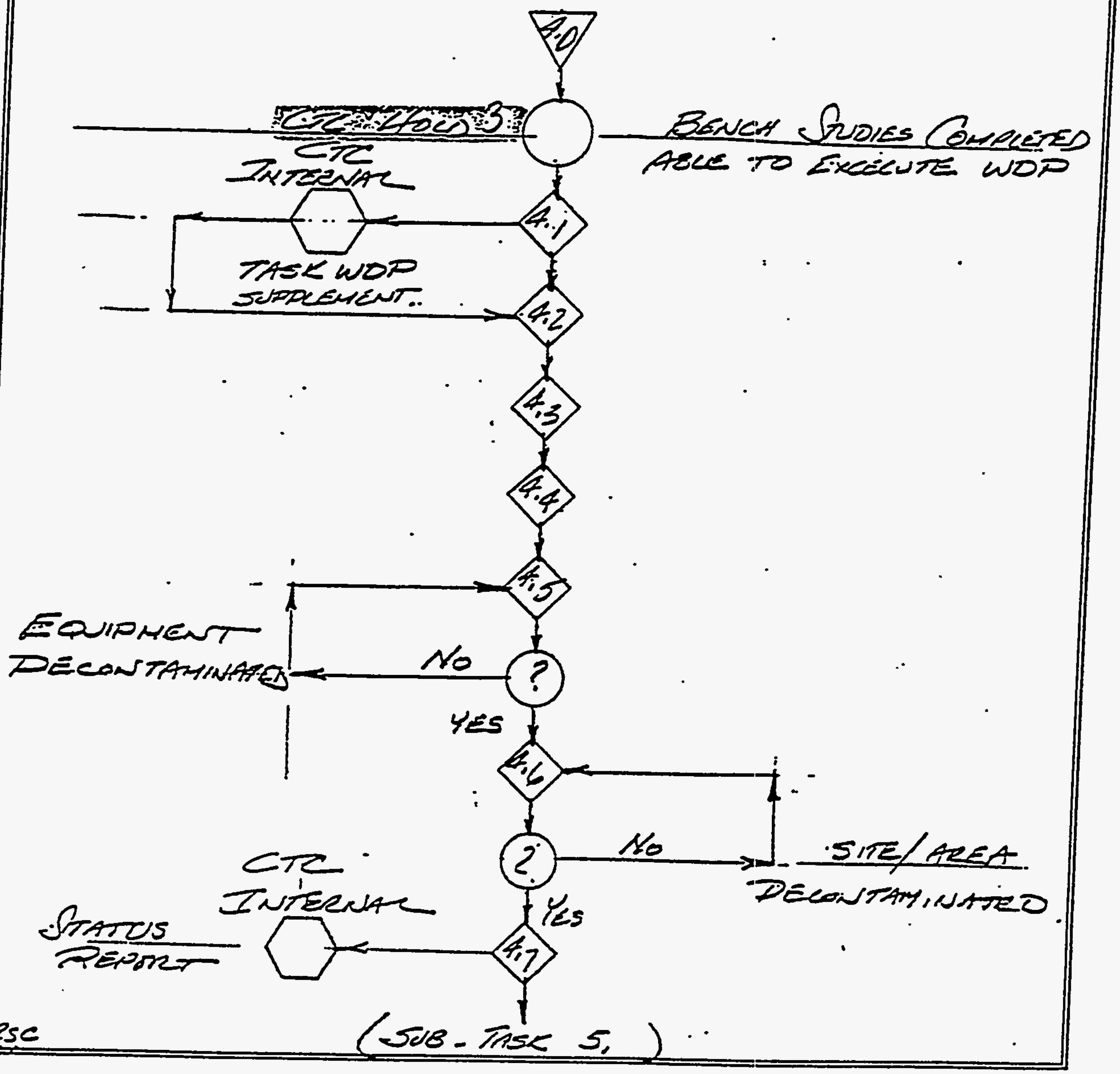
Mound Phase II, Task 7 **Waste Stabilization Studies**	**Rev. No.** (_1_1_)	



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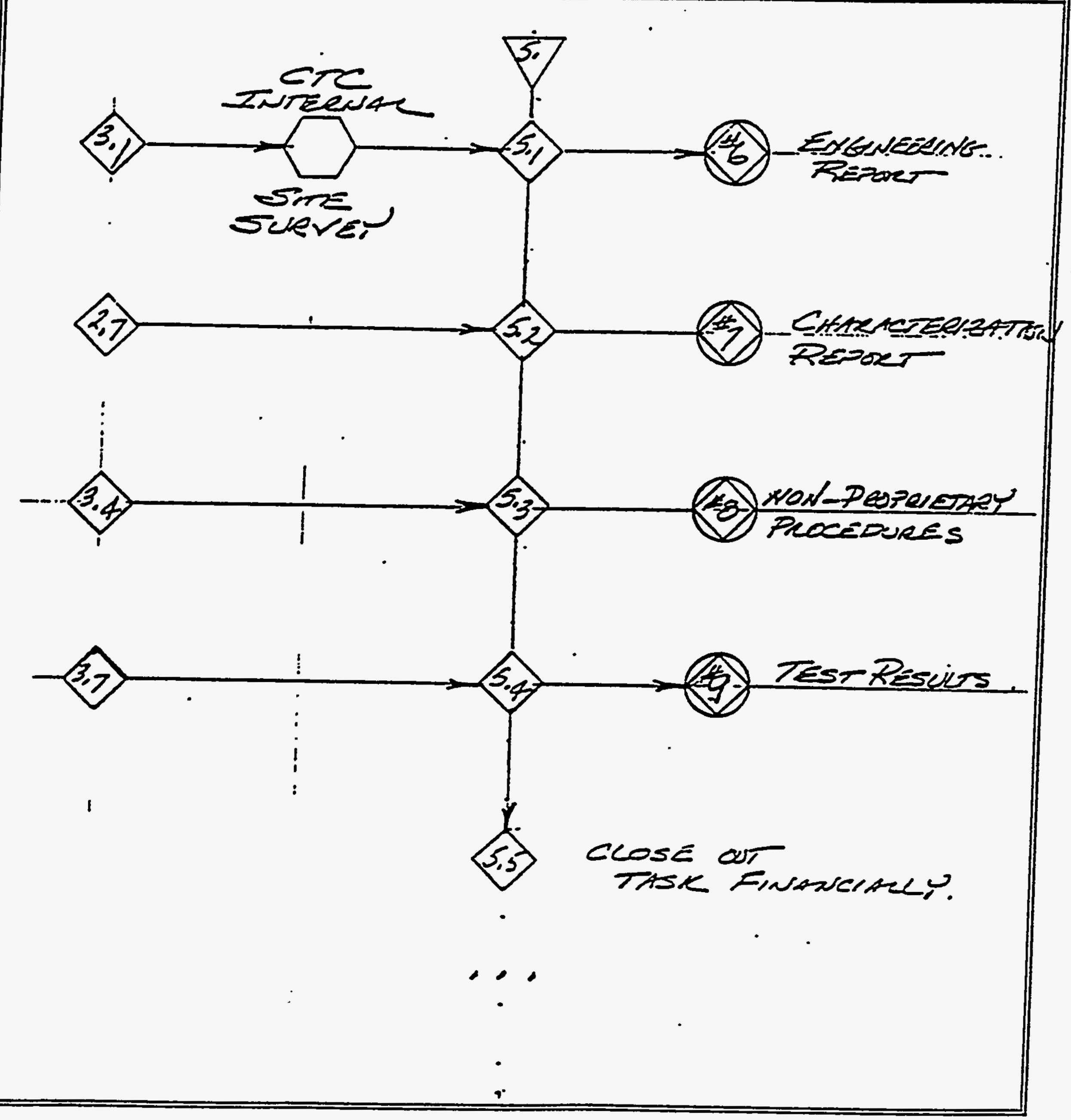

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APPENDIX B

B-1/4

RUST - Clemson Technical Center, Inc. **FACSIMILE**

PLEASE DELIVER THE FOLLOWING PAGE(S) TO:

Name ______________________ Date ______________________

Company ______________________

Fax Number ______________________

Total No. of Pages (including cover sheet) ______________________

If you do not receive all pages or have any problem with receiving this transmission, please call:

Name ______________________

Telephone Number: (803) 646-2413 Ext: ______________________

INSTRUCTIONS:

To ship TREATABILITY SAMPLES to RUST-CLEMSON TECHNICAL CENTER, please perform the following:

1) Fill out and return the attached TREATABILITY PROJECT REVIEW/ACCEPTANCE FORM via FAX (Fax # 803-646-5311) or mail to the attention of DAVID McCARTNEY (use same address as in item three of these instructions);

2) Following CTC's review and approval of the TREATABILITY PROJECT REVIEW/ACCEPTANCE FORM (allow several days), CTC will provide you with a shipping authorization number;

3) Upon receipt of the authorization number, ship the material to the address indicated here:

RUST - CLEMSON TECHNICAL CENTER
CLEMSON RESEARCH PARK
100 TECHNOLOGY DRIVE
ANDERSON, SC 29625

Please be sure to write the authorization number both on the shipping paperwork and on the shipping containers;

4) Include a completed chain-of-custody form along with the sample shipment. A blank chain-of-custody form is also attached.

5) Upon sample shipment, FAX a copy of the shipping papers to the attention of David McCartney.

/mob rev.3\29\93

b:\faxinst

B-2/4

CLEMSON TECHNICAL CENTER, INC.
TREATABILITY PROJECT REVIEW AND ACCEPTANCE FORM

Prepared by ____________________ Date ____________________
Organization ____________________ Phone ____________________

1. Source of Sample (Facility) ____________________
(City & State) ____________________

Rad. Mat. Lic. No. ____________________ EPA ID# ____________________

2. Sample Description (ex. Lagoon Sludge from Pond 001, etc.) ____________________

3. Primary Sample Constituents and Approximate Concentrations ____________________

4. Sample Hazard Assessment
   - a. Is the sample radioactive? __________ (If yes, attach listing of radioactive constituents and activity levels.)
   - b. Is the material a listed hazardous waste? __________ (If yes, indicate listing code(s) ____________________)
   - c. Is the material a characteristic hazardous waste? __________ (If yes, indicate characteristic code(s) ____________________)
   - d. Is the material an acute hazardous waste per 40CFR 261.33e? __________
   - e. Is the material a debris, soil or water contaminated with an acute hazardous waste? __________
   - f. Does the sample contain dioxins or furans? __________
   - g. Does the sample contain PCBs? __________
   - h. Does the sample have a strong incidental odor? __________
   - i. Is the sample an oxidizer, water reactive, or present hazards not mentioned above? __________ (If yes, attach explanation.)

5. Treatability Technologies to be employed:
____ Stabilization ____ Soil Washing ____ Thermal Desorption ____ Filter/Dewater ____ Other (explain) __________

6. No. of samples expected ____________________ Quantity of Sample (Kg) per Shipment ____________________

7. Planned Fate of
   - a. Unused sample ____________________
   - b. Treated Residuals ____________________
   - c. Analytical Lab/Contact Waste ____________________

8. Analytical support required (list parameter and approx. no. of analyses) ____________________

9. Anticipated Project Start Date ____________________ Anticipated Project Duration ____________________

For Clemson Technical Center Use Only
CTC Approval and Date
Project Manager ____________________ Date ____________________
Manager ESS ____________________ Date ____________________
TD&D ____________________ Date ____________________

Authorization Number ____________________

Approved by RLM Date 5-18-93 Ver. 1 Rev.2

Clemson Technical Center, Inc.

Clemson Research Park
100 Technology Drive
Anderson, SC 29625
(803) 646-2413
Fax # (803) 646-5311

CHAIN-OF-CUSTODY RECORD

Page ____ of ____

Client ______________________________
Location ______________________________
Project/Number ______________________________
Sample Type(s) ______________________________

SAMPLE IDENTITY	DATE SAMPLED/TIME	LIMS NUMBER	SAMPLE CONTAINER DESCRIPTION									REMARKS
											TOTAL	

Total No. of Containers ____

Sampled By ______________________________

Relinquished by: ____________________ Organization: ____________________ Received by: ____________________ Organization: ____________________
Date: ____________ Time: ____________ Date: ____________ Time: ____________

Relinquished by: ____________________ Organization: ____________________ Received by: ____________________ Organization: ____________________
Date: ____________ Time: ____________ Date: ____________ Time: ____________

Relinquished by: ____________________ Organization: ____________________ Received by: ____________________ Organization: ____________________
Date: ____________ Time: ____________ Date: ____________ Time: ____________

Delivery Method: ______________________________ (attach shipping bill, if any) Shipping Container ID ______________________________

8-3/4

CLEMSON TECHNICAL CENTER
SAMPLE ANALYSIS REQUEST FORM (SARF)

B-4/4

INITIATOR: ____________________
DATE: ____________________

CLIENT: ____________________

RADIATION PRESENT? YES ______ NO ______
(If Yes Attach Results)

ADDRESS: ____________________
____

RAD LICENSE NUMBER: ____________________

STD QAPjP: ______ OTHER (See Attached) ______

PHONE: ____________________

PROJECT NAME ____________________
PROJECT NUMBER: ____________________

P.O. / AUTHORIZATION #: ____________

RESPONSIBLE PARTY / CLIENT CONTACT: ____________

MAIL REPORT TO: ____________________
(If Different From Above)

DATE TO ARRIVE: ____________________
DATE RESULTS DUE FROM LAB: ____________

DATE RESULTS DUE TO CLIENT: ____________
NUMBER OF SAMPLES: ____________

SAMPLE I.D.	MATRIX	PARAMETERS REQUESTED

ADDITIONAL COMMENTS: ____________________
____

SAMPLE/MATERIAL DISPOSAL: ____________________

SUBCONTRACT TO: ____________________
PARAMETERS: ____________________
____
____

QUOTE NO.: ____________________

TD&D PM APPROVAL: ____________________ DATE: ____________

PROJECT MANAGER APPROVAL: ____________________ DATE: ____________

LAB MANAGER APPROVAL: ____________________ DATE: ____________

AF 1

FORM APPROVED BY: ____________ DATE: 3/18/93
VER.3 REV. 3/93

RRS - Clemson Technical Center

APPENDIX C

C-114

RUST - C T C **T D & D Memo**

August 09, 1993

To:	Debbie Browning	Location:	Columbia
From:	Bob Cooper	Location:	Clemson

cc:
Lew Goodroad
Bob Hemmings
Jim Huffman
AL Meyer
Mike Wetzel
Mound Project File (892032.04)
Neil Swift (Bradtec-Atlanta)

Subject: MOUND STABILIZATION, TASK 7

Deb:

As discussed, the likely waste form will be MAG*SEP℠ Particles. We have revaluated the amount of materials CTC will require for the stabilization program. Our calculations are based on our understanding from Bradtec as to the waste form and a reduced "Metals Only" TCLP analysis of the stabilized materials.

The total MAG*SEP℠ material required is 1950. grams on a dry basis. This value includes a 15 % contingency. While this is a significant reduction in the amount of the materials required, it is still in excess of the usual amount of the materials generated by Bradtec in their laboratory by almost 2 orders of magnitude.

Material acquisition must be considered an un-resolved issue at this point.

If you have any questions regarding the attached calculations please contact me.

Bob

C-2/4

RRS - Clemson Technical Center, Inc. **Calculations & Documentation**	Issued	Page
Mound Phase II, Task 7 Waste Stabilization Studies	Rev. No. (8/9/93) 1	

WASTE FORM REQUIREMENT ESTIMATE

	MASS*SEP QTY.
A. CEMENTATION STABILIZATION	1347.0
B. VITRIFICATION STABILIZATION	345.0
SUBTOTAL	1692.0
C. CONTINGENCY (@15%)	254.0
TOTAL	1946.0

1950 GRAMS SHOULD BE REQUESTED

08/09/93

C-3/4

RRS - Clemson Technical Center, Inc. Calculations & Documentation	Issued	Page
Mound Phase II, Task 7 Waste Stabilization Studies	Rev. No. ①	8/9/93

BASIS: ANTICIPATED "WASTE FORM" FROM BRIOTEC-UK WILL LIKELY BE MAG SEP PARTICLES. PER N. SWIFT 07-28-93.

	A. CEMENTITION STABILIZATION MATRIX				PROPORTION MAG SEP ④	QUICK LEACH SAMPLES	QUICK LEACH MAG SEP REQ'D PER SAMPLE (EA. SAMPLE 12 GRAMS) (IN GRAMS) a	b	c	d	TCLP SAMPLES ⑤ (EACH 100 GRAM) MAG SEP REQ'D a	b	c	d	TOTAL MAG SEP REQ'D.	
1. CEMENT PROPORTION ①	0.25	0.5	0.75	1.0	1.0	EA. OF 4	9.6 g	8. g	6.9 g	6. g	80.	66.7	57.5	50.0	254.2	376.2
						ALL 4	38.4	32.0	27.6	24.					122.0	
2. CEMENT PROPORTION	0.5	0.5	0.5	0.5	1.0	EA. OF 4	7.5 g	7.1 g	6.7 g	6.3 g	62.5	59.2	55.8	52.5	230.	340.4
LIME PROPORTION ②	0.1	0.2	0.3	0.4		ALL 4	30.0 g	28.4 g	26.8	25.2					110.4	
3. MORTAR MIX PROPORTION ③	0.25	0.5	0.75	1.0	1.0	EACH OF 4	9.6 g	8. g	6.9 g	6. g	80.	66.7	57.5	50.0	254.2	376.2
						ALL 4	38.4	32.0	27.6	24.					122.0	
															1092.8	⑥

① ASTM TYPE I, CSA NORMAL (0.5# H2O PER # CEMENT)
② HIGH CALCIUM (<5% MAGNESIUM OXIDE) QUICK LIME.
③
④ MAGNETIC SEPARATION PARTICLES WHICH HAVE PLUTONIUM CONTAINED THEREIN.

⑤ 7 DAY STRENGTH DETERMINED FOR EACH SAMPLE BY POCKET PENETROMETER PRIOR TO SAMPLE SUBMISSION FOR TCLP ANALYSIS.

⑥ FOR A DUPLICATE SET OF 4 BILLETS, EACH 100 gm, TO SEND TO ARGONNE ADD 254.2 gr MAG SEP PARTICLES TO THIS TOTAL.

8/9/93

C-4/4

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Calculations & Documentation
Mound Phase II, Task 7
Waste Stabilization Studies
Issued
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B. VITRIFICATION STABILIZATION MATRIX

			PROPORTION MAG+SEP ②	SAMPLE SIZE ③	PER SAMPLE MAG+SEP REQUIRED	NUMBER OF ④ SAMPLES	TOTAL MAG+SEP REQUIRE'T.
1.	SILICA PROPORTION ①	1.5	0.5	100 gm	25 gm	3	75 gm
2	SILICA PROPORTION	1.5	1.0	100 gm	40 gm	3	120 gm
3.	SILICA PROPORTION	1.5	1.5	100 gm	50 gm	3	150 gm
							345 gm

① SiO_2
② MAGNETIC SEPARATION PARTICLES WHICH HAVE PLUTONIUM CONTAINED THEREIN.

③ FOR TCLP TESTING METALS ONLY.
④ 1) TCLP TESTING
2) DUPLICATE
3) ANL BILLETS.

Mound-ACT*DE*CON^{SM} Feasibility Study, Phase II: Final Report

Chapter IV

Task 13 Dewatering Study of ACT*DE*CON^{SM}-Treated Sediments from the Mound Site

Prepared by

John R. North
RUST Federal Services, Inc.

December 1994

Contents

Tables

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Chapter IV

Task 13 Dewatering Study of ACT*DE*CON^{SM}-Treated Sediments from the Mound Site

by

John R. North
RUST Federal Services, Inc.

Summary

A cooperative effort by SELENTEC, Bradtec Ltd., RUST Federal Services, Inc., and Argonne National Laboratory is under way to develop and demonstrate the ACT*DE*CON^{SM} process for the remediation of plutonium-contaminated sediment (soil) from the Miami-Erie Canal at the Mound Laboratory in Miamisburg, Ohio. A phased approach is being used in this program, with the final phase (IV) consisting of the remediation of the contaminated areas at the Mound site. The work described in this chapter was performed as part of Task 13 of Phase II.

The goal of this work was to determine the most promising methods of dewatering the ACT*DE*CON^{SM}-treated soil, both in-situ and ex-situ, to allow the extractant solution and entrained contaminants to be easily removed from the soil. The laboratory tests involved the use of chemical (flocculants) and physical additives, both singly and in tandem, to determine the combination(s) that had the best chance for success in future ex-situ and in-situ experiments.

Approximately 35 tests were conducted in bench-scale and small pilot-scale pressure (and vacuum) filtration equipment. The tests focused solely on the hydraulic parameters of the dewatering process, primarily the filtration time, filter-cake quality, and filtrate quality. The removal of target species (e.g., radionuclides or simulants) from the soil matrix during the dewatering and washing process was beyond the scope of this work. All of the testing was conducted at ANL by John North (RUST Federal Services, Inc.), Yisun Cheng (RUST Environment and Infrastructure), and M. Cristina Negri (Argonne National Laboratory).

The test results showed that the ACT*DE*CON^{SM}-treated Mound sediments could be effectively dewatered by using conventional ex-situ methods. Pretreatment of the slurry with ferric chloride and lime reduced the dewatering time by a factor of 20-30 while producing a firm, high-solids-content filter cake and a relatively clear filtrate. A scale-up analysis indicated that readily available, large-scale, plate-and-frame filter presses would be feasible for this application.

Further testing, under simulated field conditions (gravity drainage), will be required to assess the feasibility of conducting the remediation in-situ. In-depth testing of the effects that the

recommended dewatering aids have on the removal of radionuclides from the soil/sediment will also be required.

IV.1 Introduction

A cooperative effort by SELENTEC, Bradtec Ltd., RUST Federal Services, Inc., and Argonne National Laboratory (ANL) is under way to develop and demonstrate the ACT*DE*CON^{SM} process for the remediation of plutonium-contaminated soil/sediment from the Miami-Erie Canal at Mound Laboratory in Miamisburg, Ohio. A phased approach is being used in this program, with the final phase (IV) consisting of the remediation of the contaminated areas at the Mound site. The work described in this report was performed as part of Task 13 of Phase II. The goal of this work was to determine the most promising methods of dewatering the ACT*DE*CON^{SM}-treated soil, both in-situ and ex-situ, to allow the extractant solution and entrained contaminants to be easily removed from the soil.

The ACT*DE*CON^{SM} process, a proprietary chemical-dissolution process that specifically targets radionuclides and other metals, is primarily used for soil-washing types of applications. Therefore, effective dewatering of the treated Mound sediment is necessary to separate and recover the wash solution (and solubilized plutonium) from the solids. The nature of the Mound soil makes dewatering difficult, however, because approximately 80% of the soil particles are less than 32 μm in size, and about 33% are smaller than 2 μm. Such a fine silt and clay matrix does not drain very well by itself, so the removal of the solubilized contaminants without the use of some type of additive(s) would be very inefficient. Furthermore, a preliminary assessment of the treated and dewatered Mound soil with respect to the revegetation studies does not appear to be very favorable. It is surmised that some type of additive or amendment will be required to enhance the soil properties and structure. The laboratory tests described below were designed both to provide better dewatering characteristics and to produce a final treated soil that is capable of sustaining vegetative growth.

IV.2 Objectives/Goals

As stated in the Introduction, most of the contaminated Mound soil/sediment consists of fine silt and clay particles. In general, silts and clays exhibit very low permeabilities and tend to retain water (and dissolved contaminants). Therefore, filter aids are usually required to enhance the dewatering of these types of materials. The filter aids can be solid additives, such as diatomaceous earth, perlite, sand, gypsum, and organic materials (compost, peat moss, etc.), which physically change the particle-size distribution of the material, thereby increasing its permeability/porosity. The filter aids can also be characterized as flocculants or coagulants, such as iron and aluminum salts, lime, and polyelectrolytes. The polymeric flocculants typically adsorb the small particles in forming larger-size flocs, while the coagulants tend to reduce the repulsive electrochemical forces between the small soil particles, allowing them to coagulate into larger particles. As a result, the dewatering of the soil/sediment is effectively enhanced.

The objective of this work was to determine the types and amounts of additives that would be required to effectively dewater and wash the ACT*DE*CON^{SM}-treated soil, for both in-situ and ex-situ scenarios. The greater part of the results were qualitative in nature. Quantitative results with respect to contaminant removal efficiency will be obtained in later phases of the project.

IV.3 Mound Soil Characteristics

Previous results from the analysis of the Miami-Erie Canal sediments are summarized here to provide some background on their physical characteristics and the nature of the contamination. The data were compiled from the following sources:

A. Rogers, D.R., 1992, "Properties of Pu-238 Contaminated Clay Deposits in the Miami-Erie Canal," EG&G Mound Applied Technologies, Miamisburg, Ohio. Prints of slide-show compilation of data by D.R. Rogers and others.

B. Brown, K.A., R.R. Heinrich, D.O. Johnson, and D.E. Edgar, 1992, "Preliminary Laboratory Study of Plutonium-238 Dissolution from Mound Soil by Means of the ACT*DE*CON^{SM} Process," Argonne National Laboratory report ANL/ESD-15, April.

C. Analytical Report — Chemical Analysis of Mound, Fernald Soil Samples (duplicate analyses at ANL). Date Analyzed: July 26, 1993. Analyst: Taylor.

The primary physical characteristics of the soil that affect the dewatering are particle-size distribution and particle-surface properties. The results from four different analyses of this material are summarized in Table IV.1, with a graphical representation shown in Figure IV.1. The graphical data show that the results from the four analyses are relatively consistent. On the average, about 90% of the soil particles are smaller than 63 µm, and 30% are less than 2-3 µm. Further details on other chemical and physical characteristics of the soil/sediment can be found in Appendix IV.A, which contains copies of the pertinent data from the sources listed above.

TABLE IV.1 Particle-Size-Distribution Data — Miami-Erie Canal Sediments[a]

	Source A		Source B		Source C - #1		Source C - #2	
Particle Size (µm)	Interval percent greater	Cumulative percent passing	Interval percent greater	Cumulative percent passing	Interval percent greater	Cumulative percent passing	Interval percent greater	Cumulative percent passing
840	1.9	98.1						
250	4.0	94.1						
125	2.8	91.3						
100					15.0	85.0	10.0	90.0
63			0.0	100.0	0.0	85.0	0.0	90.0
53	3.7	87.6						
44			11.0	89.0				
32			6.0	83.0	6.3	78.8	8.8	81.3
22			11.0	72.0				
20	22.2	65.4						
17			4.0	68.0	11.3	67.5	12.5	68.8
11			8.0	60.0				
9					20.0	47.5	18.8	50.0
8.5			8.0	52.0				
6			4.0	48.0				
5	28.4	37.0			15.0	32.5	16.3	33.8
4.3			8.0	40.0				
3.2			3.0	37.0				
3					0.0	32.5	0.0	33.8
2	7.2	29.8						
1.3			5.0	32.0				
0.9			2.0	30.0				
pan	29.8		30.0		32.5		33.8	
Total %	100.0		100.0		100.0		100.0	

[a] Source A: Slide show data compilation by D.R. Rogers (1992).
Source B: ANL Report ANL/ESD-15, by K.A. Brown et al. (1992).
Source C: Analytical report by Taylor (1993).

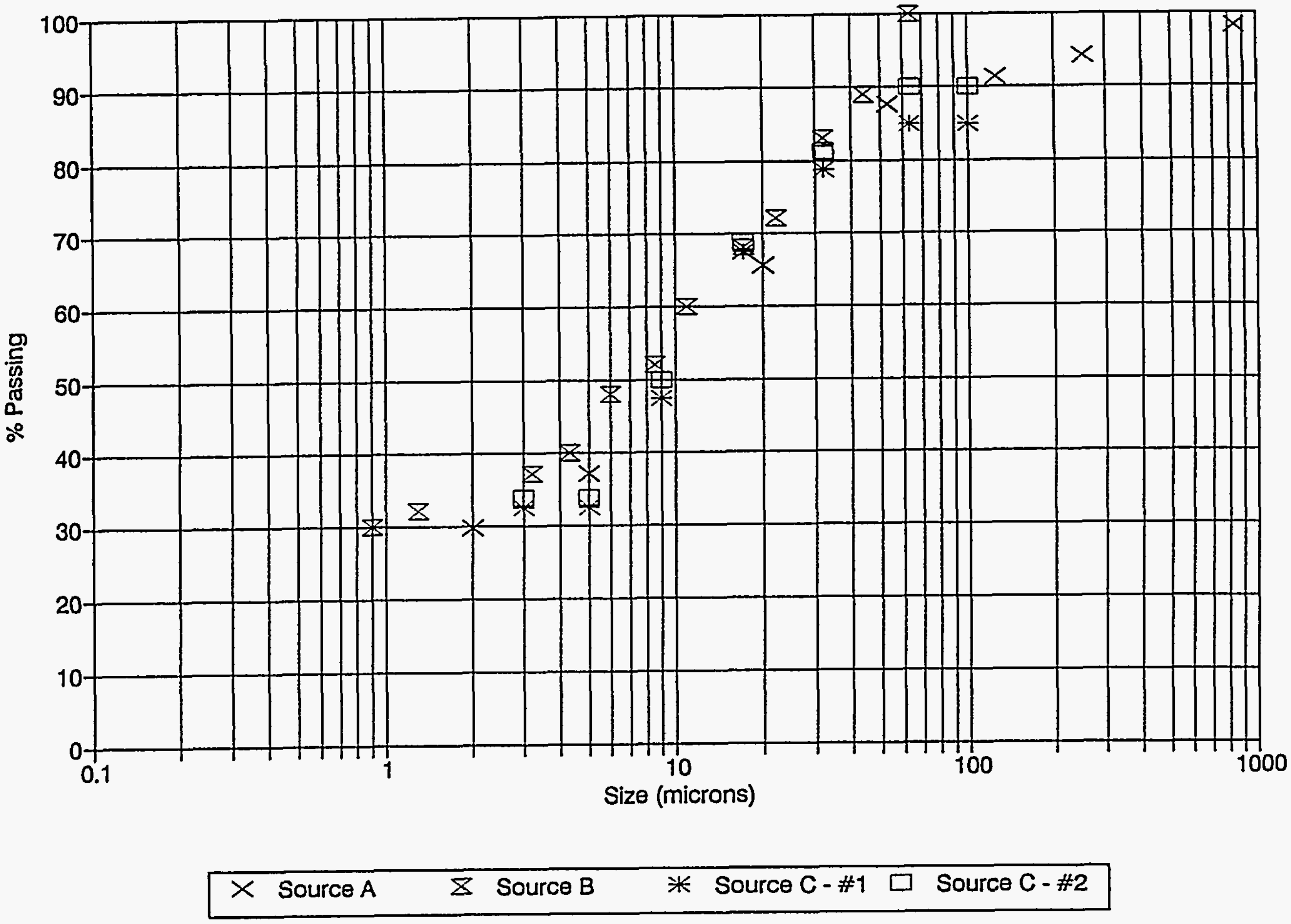


FIGURE IV.1 Particle-Size Distribution for Miami-Erie Canal Sediments

IV.4 Testing Operations and Results

In most ex-situ operations, flocculants and/or coagulants are added to soils/sludges containing significant percentages of small particles to enhance their dewatering. The ultimate goal of this project is to perform in-situ remediation, and flocculation/coagulation alone may not provide satisfactory results because these processes normally require controlled mechanical mixing to be effective. Hence, it was assumed that an inert solid additive would be required to increase the porosity/permeability of the sediment. This additive could also serve the secondary purpose of enhancing the soil's properties with respect to revegetation efforts. Therefore, the laboratory tests involved the use of flocculants/coagulants and physical additives, both singly and in tandem, to determine the combination(s) that had the best chance for success in future ex-situ and in-situ experiments. All laboratory tests were conducted at ANL.

In all of the tests, the primary measure of the effectiveness of the treatment was the time required for the material to dewater, as noted by the breakthrough of air in the filtration apparatus. Other qualitative measures included the texture and strength of the filter cake and the clarity of the filtrate. A few quantitative measurements, such as percent solids (cake) and pH and conductivity (filtrate), were made in some tests. The primary variables studied in the tests were as follows:

- **Type of Additive:** Testing of a variety of physical (bulking) agents and/or flocculants/coagulants (metal salts or polyelectrolytes);

- **Amount of Additive:** Variation of the quantity of additive required to achieve effective dewatering, measured as a percentage of the soil slurry by weight;

- **Driving Force:** Variation of the pressure/vacuum used as the driving force in the dewatering apparatus; and

- **Washing:** Examination of the effects of one or more washings of the initially dewatered solids with clean water.

IV.4.1 Starting Material

The starting material for all of the dewatering tests consisted of a surrogate slurry of the Mound soil/sediment and the ACT*DE*CON^{SM} washing solution. Two drums of clean (uncontaminated) sediment were taken from an area in the Miami-Erie Canal that was adjacent to the contaminated zone. This material was screened to less than 6 mm in size and air-dried prior to analysis and use.

The ACT*DE*CON^{SM} formulation for the dewatering tests was based on the optimal results from the dissolution tests conducted during Phase I and other parts of Phase II of the project.

The surrogate slurry of the ACT*DE*CON^{SM}-treated soil was made by mixing equal parts, by weight, of the screened sediment and the ACT*DE*CON^{SM} solution to give a 50% solids slurry. This high solids content was based on the efforts to reduce the ratio of the wash solution to the sediment that was being evaluated in the dissolution experiments. After the sediment and wash solution were combined, the pH of the slurry was adjusted to between 9 and 10 by using a concentrated sodium hydroxide solution. The slurry was then ready for testing.

IV.4.2 Preliminary Vacuum-Filtration Tests

A few initial dewatering tests were performed by using a Buchner funnel with vacuum as the driving force. It was during these tests that the difficulties in dewatering and washing the ACT*DE*CON^{SM} slurry were confirmed. Five tests were conducted over the period of August 23-25, 1993. The procedure used was as follows:

> **Part A - Initial Dewatering:** In all of the tests, approximately 100 g of the slurry was added to the Buchner funnel. The vacuum was applied and the slurry was allowed to filter, with the end time recorded.
>
> **Part B - First Washing:** After a small sample of the cake was taken for solids analysis, the remaining cake was reslurried with deionized water to again produce a slurry containing approximately 50% solids. The treatment reagent, if applicable, was added to the slurry, and the mixture was filtered.
>
> **Part C - Second Washing:** Same procedure as in Part B.

Figure IV.2 provides a comparison of the dewatering times for the various treatments that were used. A description of the treatments for the initial dewatering (A) plus two successive washings (B and C) for each test are provided in Table IV.2. The results of these tests are listed in Table IV.3.

The time required for the initial dewatering of the slurry was relatively consistent for all five tests, ranging from 6 to 9 min. The major difference between the treatments became apparent in the washing of the treated sediment. In the control test (#1), the time required to dewater the slurry in successive washings increased tremendously, to 36 and 58 min, respectively. This increase occurred even though fewer solids were present in each of the successive washings, because of the amounts removed for solids analyses.

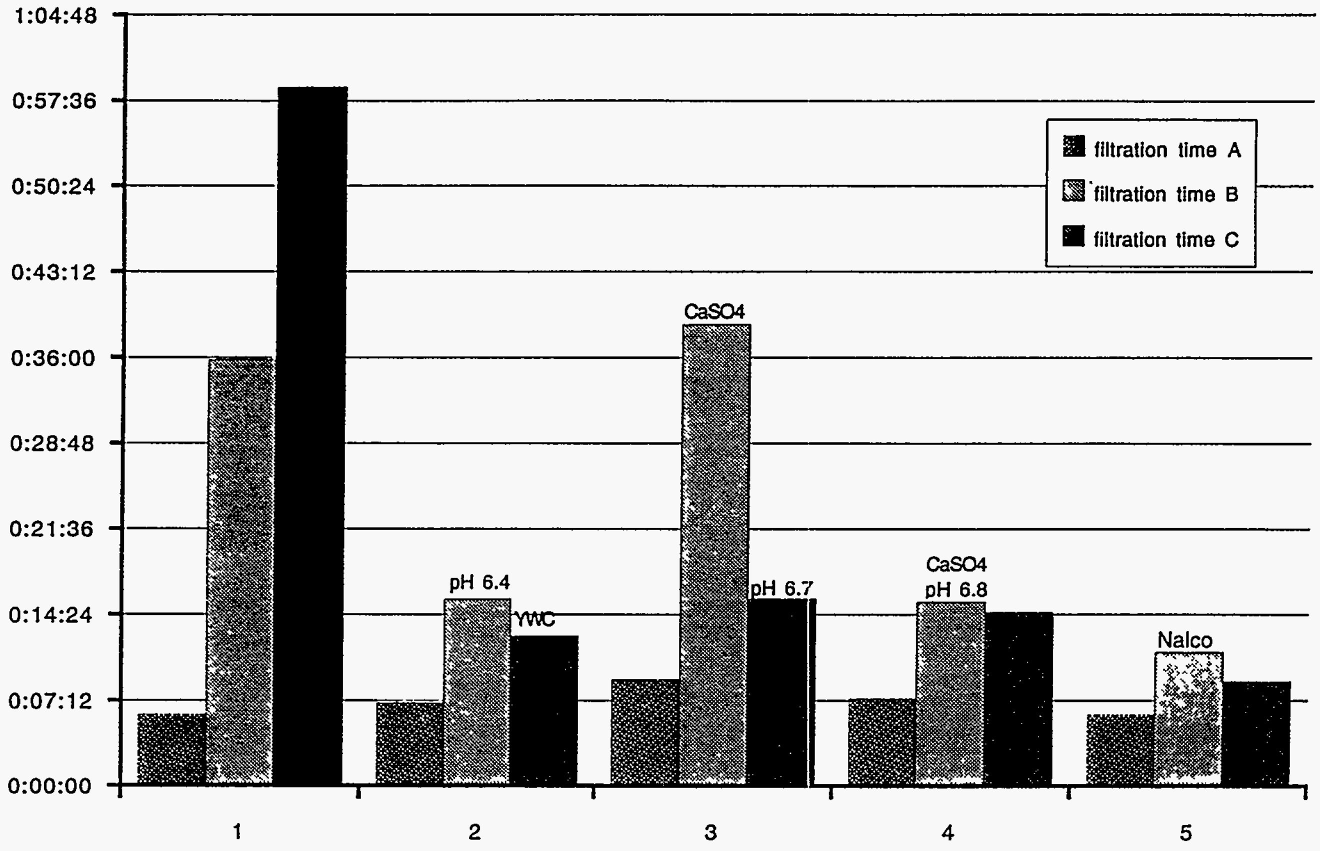


FIGURE IV.2 Dewatering Times from Vacuum-Filtration Tests

The adjustment of the washing solution pH to below 7 also showed a consistent result in three tests, lowering the dewatering time to about 15 min. The addition of yard waste compost (YWC) in test 2C appeared to give a promising result, with the dewatering time reduced to about 12.5 min. However, this result could be due to the residual effect of the pH adjustment in test 2B, which was also noticed in tests 4B and 4C. The addition of calcium sulfate ($CaSO_4$) was judged to have little or no effect, possibly because of the low dosage used.

The most dramatic effect on dewatering time was seen in test 5, in which the Nalco polymer was added. The time required to filter the first and second washings was reduced to less than 12 min. On the basis of these results, the use of polymers showed promise for further tests.

TABLE IV.2 Treatment Description for Preliminary Vacuum-Filtration Tests

	Treatments/Additives		
Test No.	Initial Dewatering (A)	First Washing (B)	Second Washing (C)
1 (control)	none	none	none
2	none	pH[a] = 6.3	YWC[b] (2.6 g)
3	none	$CaSO_4$ (0.08 g)	pH[a] = 6.7
4	none	$CaSO_4$ (0.08 g); pH[a] = 6.8	none
5	none	Nalco 7735[c] (1 mL)	none

[a] pH adjustments made with 50% solution of concentrated sulfuric acid.

[b] YWC = oven-dried yard waste compost from ANL greenhouse.

[c] Nalco 7735 = polyelectrolyte (aluminum salt and polyquaternary amine chloride) made by Nalco Chemical Co.

IV.4.3 Pressure-Filtration Screening Tests

Twenty-seven tests were conducted in a bench-scale pressure-filtration apparatus to determine the relative (qualitative) effects of various types and quantities of additives. The additives evaluated during this series of tests included the following:

- **Physical Additives (solids)**

  Peat: peat moss obtained from the ANL greenhouse; screened to < 1/4 in. and oven dried.

  Sand: quartz sand obtained from the ANL greenhouse; oven dried.

  YWC: yard waste compost obtained from the ANL greenhouse; screened to < 1/4 in. and oven dried.

  Perlite: horticultural perlite (granular) obtained from the ANL greenhouse; oven dried.

TABLE IV.3 Preliminary Vacuum-Filtration Test Data

	Data for Test No.				
Item	1 (control)	2 (B: pH 6.3 C: YWC 5%)	3 (B: $CaSO_4$ C: pH 6.7)	4 (B: $CaSO_4$+ pH 6.8)	5 (Nalco 7735)
Filtration time A[a]	0:06:02	0:07:02	0:09:00	0:07:23	0:06:04
Filtration time B[b]	0:35:51	0:15:41	0:38:44	0:15:28	0:11:15
Filtration time C[c]	0:58:45	0:12:36	0:15:43	0:14:37	0:08:48
Initial ph A	10.2	10.06	10.35	10.05	10.28
Initial ph B	9.6	6.67	9.45	6.8	7
Initial ph C	9.38	7.4	6.67	7.45	7.6
Initial amount A (g)	101	105	106	100	103
Initial amount B (g)	89	101	89	91	100
Initial amount C (g)	68	74	82	79	66
Final cake thick A (mm)	6	6.5	5.2	6.5	5.5
Final cake thick B (mm)	4.9	5.5	5.5	5.6	5.8
Final cake thick C (mm)	4.5	5	5	4	5
Final cake mass A (g)	74	82	78	76	74
Final cake mass B (g)	62.4	65.9	65.5	64.2	61.3
Final cake mass C (g)	48.7	57	54.2	50.2	50.8
Cake dry solids A (%)	63.3	63.6	64.3	63.4	65.5
Cake dry solids B (%)	65.3	65	66.9	66.7	58.3
Cake dry solids C (%)	65.4	66.6	62.8	65.1	63.6
Volume liquid A (ml)	24	28	28	28	38
Volume liquid B (ml)	21	34	22	28	24
Volume liquid C (ml)	18	19	30	22	15
pH liquid A	9.65	9.6	9.66	10.8	9.91
pH liquid B	9.45	8.1	9.2	8.14	8.08
pH liquid C	9.3	8.24	8.12	8.25	8.2
Electrical Conductivity					
Liquid A (µmhos/cm)	7,300	5,400	7,600	6,500	6,000
Liquid B (µmhos/cm)	4,300	9,300	5,400	8,200	9,400
Liquid C (µmhos/cm)	2,500	5,900	7,600	5,400	4,300
Liquid dry solids A (%)	2.1	1.8	1.8	1.8	1.8
Liquid dry solids B (%)	1.5	1.6	1.3	1.3	1.2
Liquid dry solids C (%)	1.6	0.8	0.9	0.7	0.5
Liquid mass A (g)	62.76	67.58	59.2	68.48	70.14
Liquid mass B (g)	19.78	33.1	21.01	26.28	21.6
Liquid mass C (g)	16.54	17.2	28.2	20.2	na[d]

[a] A: initial dewatering.

[b] B: first washing.

[c] C: second washing.

[d] Not applicable.

HB900 and HB5000: perlite filter aid (powder); two different grades.

Gypsum: garden gypsum (calcium sulfate); obtained from local store.

- **Flocculants/Coagulants (aqueous solutions)**

Lime: 10% slurry of lime (calcium oxide/hydroxide).

EXCEL+: 1% solution of EXCEL+100 liquid cationic polyacrylamide flocculant; made by American Cyanamid.

572C: 1% solution of MAGNIFLOC 572C cationic polyamine flocculant; made by American Cyanamid.

Fe/Li: 20% solution of ferric chloride and 10% slurry of lime; added in equal volumes to slurry.

E-3098: 1% solution of E-3098 cationic polyacrylamide flocculant: made by American Cyanamid.

573C: 1% solution of MAGNIFLOC 573C cationic polyamine flocculant; made by American Cyanamid.

The testing equipment consisted of a 90-mm-diameter stainless steel filter holder with a 750-ml-capacity reservoir on top. The slurry to be filtered was added via a funnel through a top port on the reservoir. This port was then closed and nitrogen pressure was applied to the reservoir from a regulated cylinder. Filtrate was collected in a graduated cylinder underneath the bottom port on the filter holder. The end of the filtration cycle was noted by the breakthrough of the nitrogen (i.e., gas bubbles) in the filtrate port.

In order to keep the trials relatively consistent with respect to the thickness of the filter cake that was formed, the quantities of the slurry and additives used were varied. The goal was to keep the estimated total solids within the range of 45-50 g for the initial dewatering step. Washings were simulated by reslurrying the filter cake (from the initial dewatering step) in deionized water, and repeating the filtration. Fewer solids were available in the washings, because an estimated 5% of the material was lost during mixing and transferring in each filtration step. The primary measurement for the tests was the time required for dewatering a batch of slurry. Other parameters, such as cake structure and dryness, were observed visually.

The results from the bench-scale dewatering tests are listed in Table IV.4. The raw data consist of the weights and volumes of materials used or collected (amount), the pressure applied, the dewatering time, and the filtrate pH in some trials. The calculated values — total solids, total liquids, and estimated cake percent solids — are based on a 50% solids content for the starting slurry, estimated percent solids/moisture for the additives, and a 5% loss of material during each filtration step. Detailed discussions of the results listed in Table IV.4 are provided in Section IV.5, Discussion/Conclusions. A few general comments on the test parameters and operations are presented below:

- The testing range for the physical additives, expressed as the percentage of material added to the initial slurry used (total weight basis), varied from 3% to 70%.
- The addition range for the flocculants/coagulants, also expressed as a weight percentage of the initial slurry, varied from 7% to 50%.
- A relatively low dewatering pressure of 20 pounds per square inch gauge (psig) was used in most of the tests. The effects of pressure on the dewatering time were evaluated over a range of vacuum (estimated at -12 psig to +100 psig).
- Washings were performed in a few of the trials to determine whether the dewatering agent/aid was susceptible to washout, which would be characterized by significantly longer dewatering times in the successive filtrations.

IV.4.4 Confirmatory Pressure-Filtration Tests

A few tests were conducted in a second pressure-filtration unit that simulates the conditions of a plate-and-frame filter press. These tests were designed to confirm the results of some of the most promising of the trials (described in the previous section) in a more representative piece of ex-situ dewatering equipment. Only the flocculants or coagulants were used in these tests, because the solid bulking agents are not normally used in ex-situ situations.

A bench-scale filter press built by JWI, a leading manufacturer of filter presses, was used for these tests. The press consists of a 2-in.-diameter by 1.25-in.-thick filter chamber formed by two end plates and a frame, all made of stainless steel. These pieces are supported on a heavy-duty iron frame. Closing pressure (up to 7,000 psig) for the plates and frame is supplied by a small hand-powered hydraulic cylinder. Woven polyethylene filter cloths are inserted between the end plates and frame to serve as the filter medium.

TABLE IV.4 Mound Soil Dewatering — Summary of Pressure-Filtration Screening Tests

			Physical Additives[b]			Flocculants[b]				Approximate Totals[c]				Filtrate Data		
Test Date	Run No.[a]	Slurry Wt (g)	Type	Amount (g)	% add.	Type	Amount (mL)	% add.	H_2O (mL)	Solids (g)	Liquids (mL)	Pressure (psig)	Time (min)	Amount (mL)	pH	Est. Cake % Solids[d]
8/10/94	1	99.9	peat	10.0	10	-	-	-	30.5	57.0	76.4	20	60.0	33.0	-	56.7
8/13/94	2	49.9	sand	35.0	70	-	-	-	15.2	57.0	38.1	20	37.0	23.0	-	79.0
	3	50.5	YWC	14.6	29	-	-	-	20.1	37.9	43.1	20	13.0	18.0	-	60.1
	4	50.2	perlite	10.0	20	-	-	-	40.4	33.3	62.2	20	21.0	30.5	-	51.2
	5	50.2	YWC	24.9	50	-	-	-	29.2	49.9	51.6	20	12.0	24.5	-	64.8
			perlite	2.5	5	-	-	-	-	-	-	-	-	-	-	-
9/3/94	6	100.0	-	-	-	-	-	-	-	47.5	47.5	20	>40.0	-	-	-
	7	100.0	-	-	-	lime	10	10	-	48.5	56.1	20	4.3	27.0	-	62.5
	7A	(cake)	-	-	-	-	-	-	30.0	46.0	56.1	20	5.0	23.0	-	58.2
	8	100.0	-	-	-	lime	20	20	-	49.4	64.6	20	5.8	31.0	-	59.5
	8A	(cake)	-	-	-	-	-	-	30.0	46.9	60.4	20	6.0	25.0	-	57.0
	8B	(cake)	-	-	-	-	-	-	30.0	44.6	62.1	20	6.3	25.0	-	54.5
	9	100.0	HB900	2.5	3	lime	10	10	10.0	50.8	65.6	20	5.0	27.0	-	56.9
	9A	(cake)	-	-	-	-	-	-	30.0	48.3	65.1	20	5.3	26.0	-	55.2
	10	100.0	HB5000	2.5	3	lime	10	10	-	50.8	56.1	20	4.8	23.0	-	60.6
	10A	(cake)	-	-	-	-	-	-	30.0	48.3	59.9	20	8.5	24.0	-	57.4
	11	100.0	-	-	-	lime	10	10		48.5	56.1	VAC	6.0	31.0	-	65.9
	11A	(cake)	-	-	-	-	-	-	30.0	46.0	52.3	VAC	6.0	28.0	-	65.4
	12	100.0	-	-	-	EXCEL+	20	20	-	47.7	66.3	20	>20.0	45.0	-	69.1
	13	100.0	-	-	-	572C	15	15	-	47.6	61.6	20	20.0	33.0	-	62.5
9/8/94	14	100.0	-	-	-	Fe/Li	10	10	-	49.9	64.1	20	3.5	28.0	-	58.0
	14A	(cake)	-	-	-	-	-	-	30.0	47.4	62.8	20	3.1	27.0	-	56.9
	14B	(cake)	-	-	-	-	-	-	30.0	45.0	62.5	20	3.0	27.0	-	55.9
	15	50.0	YWC	25.0	50	-	-	-	50.0	47.5	71.3	20	10.0	-	-	40.0
	16	50.0	YWC	25.0	50	Fe/Li	10	20	30.0	49.9	68.9	20	1.5	35.0	8.7	59.6
	17	75.0	YWC	7.5	10	Fe/Li	10	13	15.0	45.1	66.5	20	3.0	31.0	9.3	56.0
	17A	(cake)	-	-	-	-	-	-	30.0	42.9	62.2	20	3.3	28.0	9.3	55.6
	17B	(cake)	-	-	-	-	-	-	30.0	40.7	61.0	20	3.5	28.0	9.3	55.2

TABLE IV.4 (Cont.)

			Physical Additives[b]			Flocculants[b]				Approximate Totals[c]				Filtrate Data		
Test Date	Run No.[a]	Slurry Wt (g)	Type	Amount (g)	% add.	Type	Amount (mL)	% add.	H_2O (mL)	Solids (g)	Liquids (mL)	Pressure (psig)	Time (min)	Amount (mL)	pH	Est. Cake % Solids[d]
9/8/94	18	75.0	YWC	7.5	10	Fe/Li	5	7	15.0	43.9	58.2	20	4.1	28.0	9.1	59.3
	18A	(cake)	-	-	-	-	-	-	30.0	41.7	57.2	20	5.1	26.0	9.1	57.2
	18B	(cake)	-	-	-	-	-	-	30.0	39.7	58.1	20	6.4	26.0	9.1	55.2
	19	75.0	YWC	7.5	10	Fe/Li	10	13	15.0	45.1	66.5	VAC	4.8	40.0	9.3	63.0
	19A	(cake)	-	-	-	-	-	-	30.0	42.9	53.7	VAC	4.0	31.0	9.3	65.4
	19B	(cake)	-	-	-	-	-	-	30.0	40.7	50.0	VAC	5.0	31.0	9.3	68.1
	20	75.0	YWC	7.5	10	-	-	-	15.0	42.8	49.9	20	45.0	29.0	-	67.2
	21	75.0	YWC	7.5	10	Fe/Li	10	13	15.0	45.1	66.5	50	1.8	32.0	9.3	56.7
	22	75.0	YWC	7.5	10	Fe/Li	10	13	15.0	45.1	66.5	100	1.4	34.5	9.3	58.5
9/23/94	23	99.1	gypsum	6.8	7	-	-	-	10.3	53.5	56.9	20	7.0	34.5	9.4	70.5
	24	75.6	YWC gypsum	7.5 3.9	10 5	-	-	-	13.0	46.7	48.3	20	3.5	29.0	9.0	70.8
	24A	(cake)	-	-	-	-	-	-	30.8	44.4	47.6	20	13.0	28.0	8.9	69.4
	25	60.0	YWC	15.0	25	E-3098	30	50	20.0	43.0	75.7	20	1.3	36.0	8.7	52.0
	25A	(cake)	-	-	-	-	-	-	30.0	40.9	66.2	20	1.0	23.0	8.7	48.6
	25B	(cake)	-	-	-	-	-	-	40.0	38.8	79.1	20	4.3	46.0	8.8	54.0
	26	60.0	YWC	15.0	25	573C	30	50	20.0	43.0	75.7	20	1.0	45.0	8.8	58.4
	26A	(cake)	-	-	-	-	-	-	40.0	40.9	67.2	20	1.3	37.0	8.8	57.5
	26B	(cake)	-	-	-	-	-	-	40.0	38.8	66.7	20	2.0	40.0	8.9	59.3
	27	60.0	YWC	15.0	25	Fe/Li	10	17	20.0	45.1	64.1	20	1.5	37.0	9.1	62.5
	27A	(cake)	-	-	-	-	-	-	40.0	42.9	63.8	20	2.3	37.5	9.1	62.0
	27B	(cake)	-	-	-	-	-	-	40.0	40.7	63.0	20	2.8	38.5	9.1	62.5

---

[a] Suffixes A and B refer to successive washings of the cake by reslurrying with deionized water and refiltering.

[b] Additives and flocculants are described in text; "% add." is the ratio of additive amount to slurry amount.

[c] Calculations for solid and liquid totals are based on 5% loss of material during slurry transfer and estimated solids contents for flocculants.

[d] Est. Cake % Solids = 100 × (Solid) / [(Solid) + (Liquid) − (Filtrate amount)].

A separate pressure vessel was used for precoating the filter cloths with diatomaceous earth and loading the press with slurry. Compressed nitrogen was applied to the top of the vessel, forcing the precoat solution or slurry through a port on the top of the frame section. Filtrate drains out of small ports on the bottom of the end plates. The end of the press cycle was indicated by a diminishing or stable flow of filtrate. Washing of the formed filter cake in the press is accomplished by forcing water through one of the end plate ports; the rinsate drains out of the other port. The air blow (nitrogen, in this case) of the cake proceeds in the same manner as the washing, after the predetermined volume of wash water (approximately three times the filter cake volume) has been pushed through the cake.

Three successful tests were conducted using the bench-scale JWI filter press. A fourth test was unsuccessful because too high a pressure was used at the start of feeding, causing blinding of the filter cloths. Two of the American Cyanamid polymers, E-3098 and 573C, and the Fe/Li treatment were tested. The data from the three trials are presented in Table IV.5. A discussion of the results is provided in Section IV.5.

TABLE IV.5 Mound Soil Dewatering — Summary of JWI Lab-Press Tests

Part A

	Results for Date - Run No.		
	9/24/94-01	10/20/94-01	10/20/94-03
Preparation data			
Amount of slurry (mL)	600	400	300
Flocculant description	1% solution of 573C	1% solution of E-3098	10% slurry of lime and 20% solution of $FeCl_3$
Flocculant amount (mL)	200	200	45 (each)
Flocculant/slurry ratio	33%	50%	15%
Precoat used	1 g d.e. (FW12)	1 g d.e. (FW12)	1 g d.e. (FW12)
Filtrate Parameters			
Final volume (mL)	48	52	61
pH	8.8	8.6	9.3
Color/clarity	light yellow/clear	yellow-orange/cloudy	yellow-orange/cloudy
Cake Parameters			
Description	Firm, solid	Very soft middle	Very hard/firm
Final weight (g)	105.5	100.4	111.4
Density (g/cm^3)	1.64	1.56	1.73
Solids determination			
Tare (g)	34.56	38.69	41.49
Gross wt - before (g)	55.39	56.15	56.47
Gross wt - after (g)	47.23	48.21	51.18
Solids content (%)	60.8	54.5	64.7

TABLE IV.5 (Cont.)

Part B

Filtration data	Time (min)	9/24/94-01 Filtrate Vol (mL)	9/24/94-01 Rate (mL/min)	10/20/94-01 Filtrate Vol (mL)	10/20/94-01 Rate (mL/min)	10/20/94-03[a] Filtrate Vol (mL)	10/20/94-03[a] Rate (mL/min)
	0	0		0		0	
	1					12	12.0
	2	16	8.0	10	5.0	18	6.0
	3	20	4.0	13	3.0	24	6.0
	4	23	3.0	17	4.0	31	7.0
	5	26	3.0	21	4.0		
	6	30	4.0			41	5.0
	7			25	2.0		
	8					48	3.5
	9	36	2.0				
	10			30	1.7	54	3.0
	12	43	2.3			58	2.0
	13			34	1.3		
	14					61	1.5
	15	48	1.7				
	16			39	1.7		
	19			46	2.3		
	22			49	1.0		
	25			52	1.0		

Results for Date - Run No.

[a] Notes for cake washing/drying for run 10/20/94-03 only.

1. Washing: 194 ml of H_2O (3.0 cake volumes) pushed through the cake at 100 psig in 11 minutes.
2. Filtrate: light yellow; slightly cloudy; pH = 9.31.
3. Air drying: 100 psig air used to dry cake; breakthrough in 3.5 min; 4 mL of filtrate eluted.

IV.5 Discussion and Conclusions

A variety of dewatering aids and processing conditions were used in tests to determine the optimal conditions for effective in-situ treatment of the ACT*DE*CON^{SM}-treated Mound sediment. However, ex-situ types of dewatering equipment were employed in the trials because of their availability and ease of operation. Relatively low pressures were used to make the tests more representative of in-situ dewatering, which would essentially rely on gravity drainage. The test results provide a comparative look at the effects of the various treatments on the dewatering time. Discussions and conclusions about the results are provided below.

IV.5.1 Screening Tests

The screening tests were designed to evaluate a number of different variables, as described in Section IV.4. Presented in this section are discussions concerning the effects of variations in these parameters with respect to the dewatering time. As a point of reference, filtration of the untreated slurry at 20 psi (Run 6) was cut off at 40 min because of the slow dewatering rate obtained. The runs used for the comparisons were chosen on the basis of their nearly equivalent solids content. The run numbers correspond to the numbering system used in Table IV.4.

IV.5.1.1 Effects of Physical Additives

Figure IV.3 provides a comparison of the following six trials in which physical bulking agents were added to the slurry:

- Run #1: 10% peat,
- Run #2: 70% sand,
- Run #5: 50% YWC and 5% perlite,
- Run #15: 50% YWC,
- Run #23: 7% gypsum, and
- Run #24: 10% YWC and 5% gypsum.

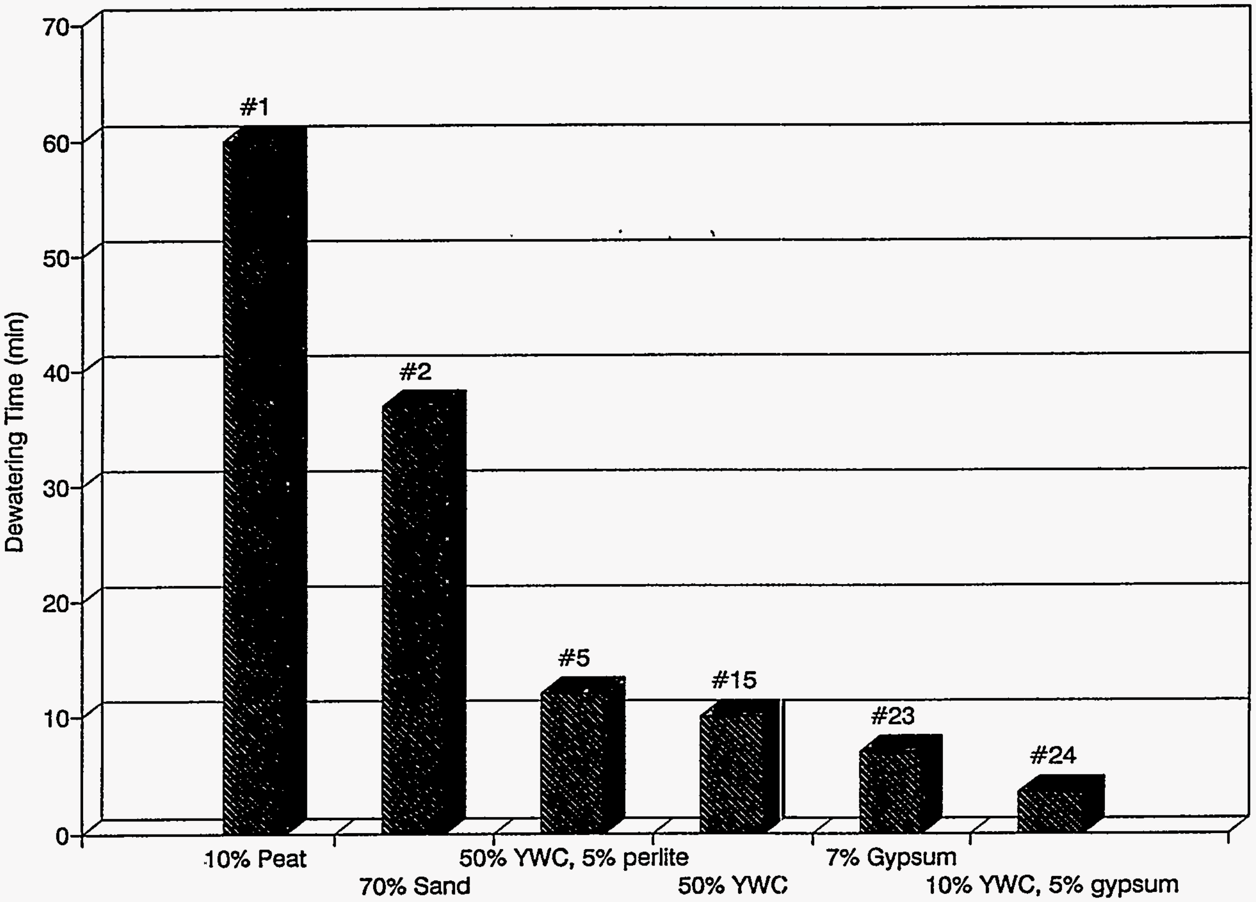


FIGURE IV.3 Effects of Physical Additives on Dewatering Times

All of these runs were conducted at 20 psig, with the total solids amounts ranging from 47 to 57 g. Pertinent features of these results include the following:

- Shortest dewatering times were observed in the two trials in which gypsum was added. The effect of the gypsum was further enhanced by the simultaneous addition of YWC: the dewatering time was cut in half — from 7.0 min (Run #23) to 3.5 min (Run #24).

- Dewatering times of 10-12 min were obtained for YWC trials — Runs #15 (YWC only) and #5 (YWC plus 5% horticultural perlite). However, the 50 wt % addition ratio was judged to be somewhat excessive. Because the YWC has a relatively low density, a fairly large volume of material would need to be added, which could cause a significant ground swell.

- Addition of 10% peat (Run #1) or 70% sand (Run #2) did very little to enhance or accelerate the dewatering process. Higher addition ratios for these materials were not tested, because larger amounts of both would present material handling problems in full-scale operations (the volume of peat would be excessive, and the sand is not recommended because of the mass required and its abrasiveness).

At first glance, the addition of gypsum appeared to show the most promise for enhancement of the dewatering process. Its potential use was diminished, however, by the results from Run #24A, which consisted of washing the cake produced from Run #24. In this run, the dewatering time increased to 13 min, compared to 3.5 min for the initial step. It appears that the gypsum is either washed out of the cake or its effects are very temporary. Therefore, gypsum was not evaluated in any subsequent trials.

Of the physical additives tested, the YWC was perceived as the most beneficial agent with respect to revegetation of the sediments because it added structure and porosity to the silt/clay. Although the YWC did show signs of being effective, the quantities required to obtain beneficial results were significant. It might be possible to use YWC at lower addition ratios in conjunction with a flocculant or coagulant. Therefore, the majority of the "combination" tests utilized YWC as the physical additive. The results of these tests are discussed in Section IV.5.1.3.

IV.5.1.2 Effects of Flocculants/Coagulants

Figure IV.4 shows the effects of various flocculants/coagulants on the slurry dewatering time for the following runs:

- Run #7: 10% lime,
- Run #8: 20% lime,
- Run #12: 20% EXCEL+,
- Run #13: 15% 572C, and
- Run #14: 10% ferric and 10% lime.

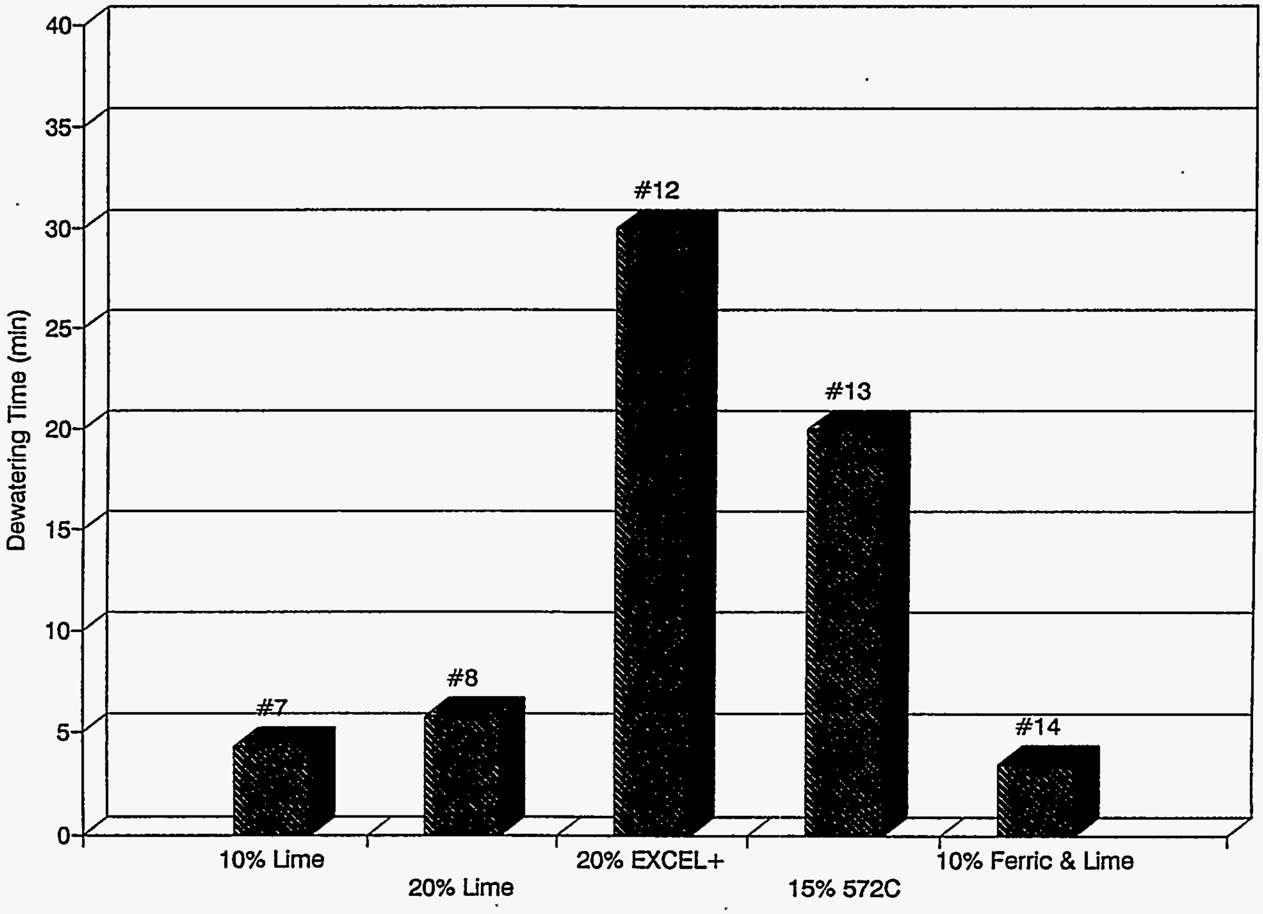


FIGURE IV.4 Effects of Flocculants on Dewatering Times

For all runs, slurry was dewatered at 20 psig; the estimated total solids in the slurry ranged from 48 to 50 g. Pertinent observations include the following:

- The use of lime and Fe/Li produced significant reductions in the dewatering time, in comparison to the results of the physical additive tests. The addition of 10% Fe/Li (Run #14) gave the best results (3.5 min for dewatering).

- When lime was added by itself, a 10% addition rate gave better results than a 20% addition rate (Run #7 versus Run #8).

- The two cationic polymers used in Runs #12 and #13 produced only marginal results (dewatering times of 20 min or more). The results indicated that these two polymers were either not suitable for this material or that their addition ratios were too small.

Successive washings of the lime or Fe/Li cakes also showed promising results. The dewatering times did not increase significantly; in fact, the time required to dewater the reslurried (washed) material decreased for the Fe/Li treatment (Run #14).

IV.5.1.3 Effects of Additive Combinations

Figure IV.5 shows the results for three trials in which the flocculants/coagulants were used in combination with a physical additive:

- Run #25: 50% E-3098 + 25% YWC,
- Run #26: 50% 573C + 25% YWC, and
- Run #27: 17% Fe/Li + 25% YWC.

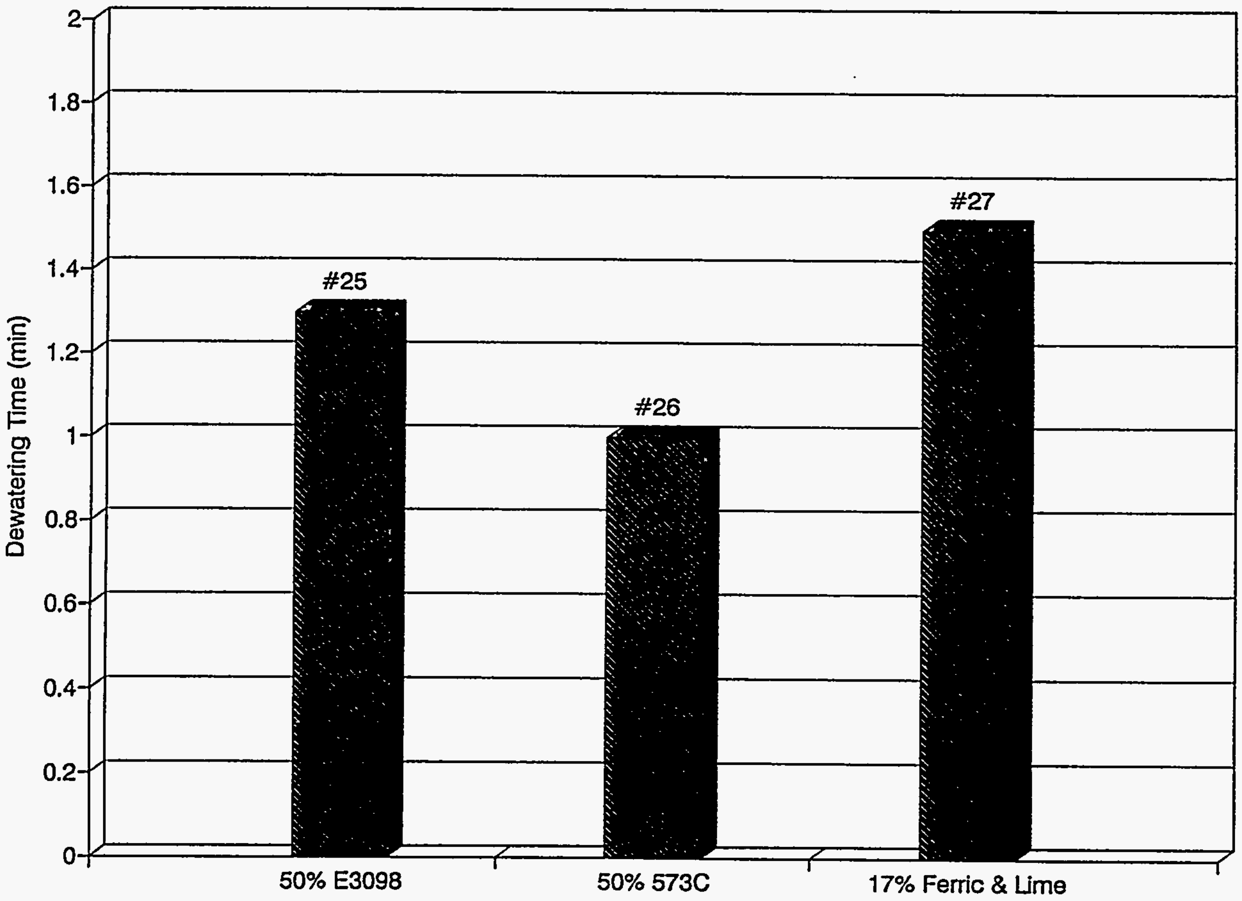


FIGURE IV.5 Effects of Adding Flocculants Plus 25% YWC on Dewatering Times

All three of these runs were conducted at 20 psig, with estimated initial solids amounts in the range of 43-45 g. Very good results were obtained for these tests; the dewatering time was less than 1.5 min for each run. All three treatments also performed relatively well in successive washings, showing only moderate increases in the dewatering time. The Fe/Li trial produced a slightly better cake than the polymer trials, with an estimated solids content of 62%.

Figure IV.6 provides a comparison of dewatering times for various combinations of Fe/Li and YWC:

Dotted Line	**Solid Line**
Run #16: 50% YWC + 20% Fe/Li	Run #17: 10% YWC + 13% Fe/Li
Run #17: 10% YWC + 13% Fe/Li	Run #18: 10% YWC + 7% Fe/Li
Run #14: 0% YWC + 10% Fe/Li	Run #20: 10% YWC + 0% Fe/Li.

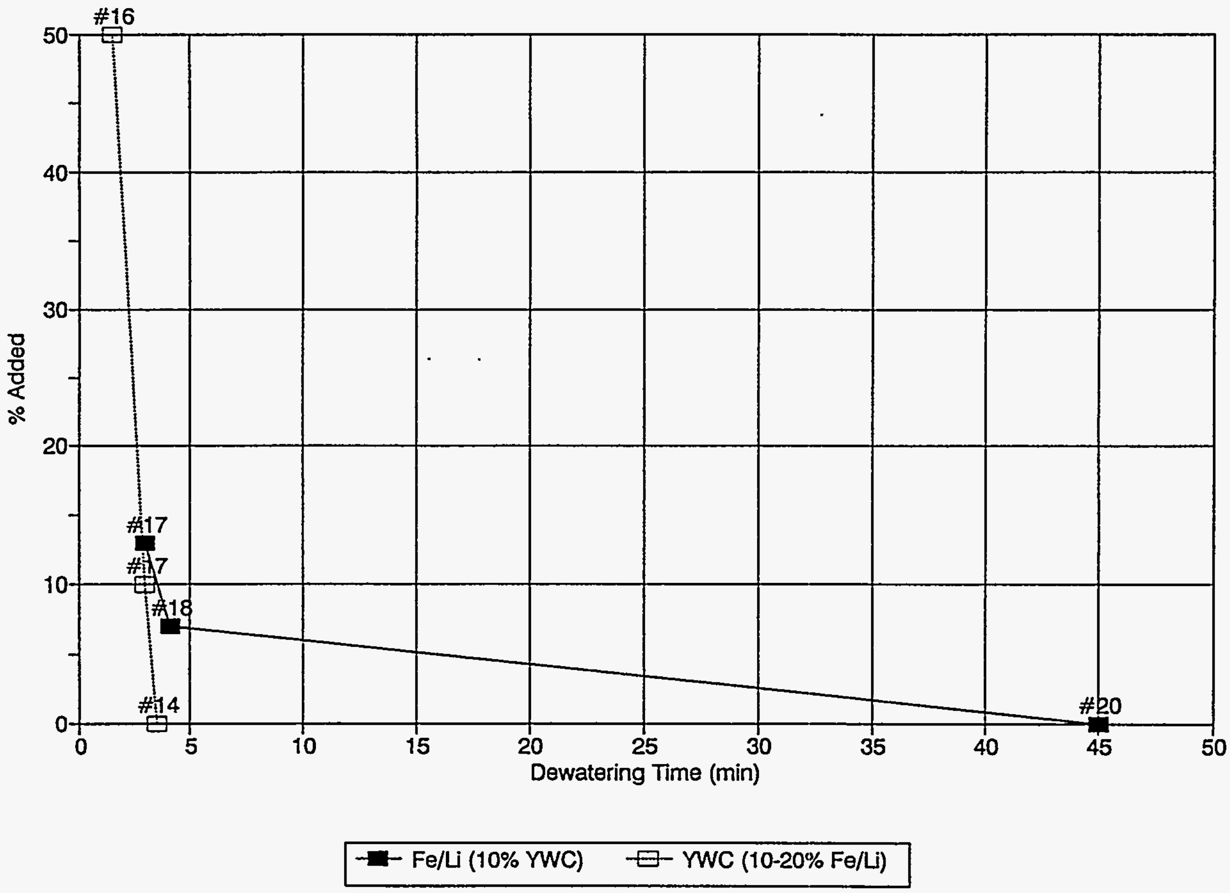


FIGURE IV.6 Effects of Adding Various Combinations of Fe/Li and YWC on Dewatering Times

All of these trials were conducted at 20 psig, with initial solids amounts in the range of 43-50 g. Figure IV.6 shows that the Fe/Li addition was the critical parameter — the dewatering time was about 4 min or less when at least 7% Fe/Li was added. For Run #20, with only 10% YWC added (no Fe/Li), the dewatering time ballooned to 45 min. Even when 50% YWC was used by itself in one trial (Run #15), the dewatering time was still about 10 min.

IV.5.1.4 Effects of Driving Force

Figure IV.7 shows the effects of variations in the filtration driving force (pressure) on the dewatering time. Four tests were conducted on identical slurries, each treated with 10% YWC and 13% Fe/Li, and each containing about 45 g of initial solids. The following pressures were used: 100 psig (Run #22), 50 psig (Run #21), 20 psig (Run #17), and vacuum (Run #19) (the vacuum was assumed to be approximately -12 psig).

The graph shows that the dewatering time is inversely proportional to the driving force used to filter the material. This result is typical for "normal" materials that contain granular particles and are essentially incompressible. Slurries that contain large percentages of silts and

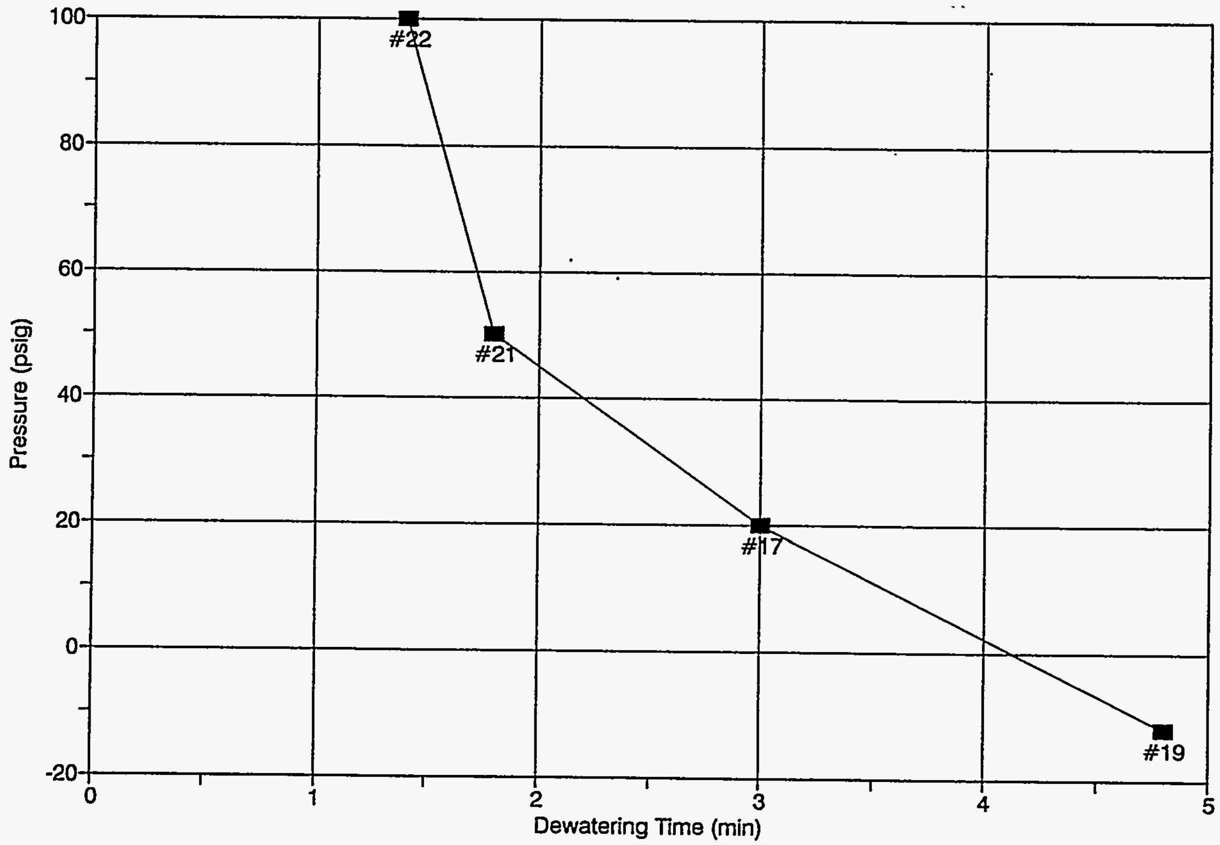


FIGURE IV.7 Effects of Pressure and Vacuum on Dewatering Time of Slurries Containing 10% YWC and 13% Fe/Li clays, such as the Mound sediments, do not always behave in this manner, because the small particles tend to compress and pack into a very tight matrix. In some cases, the dewatering time increases in proportion to the driving force, due to the high resistance to fluid flow caused by the compacted filter cake. These trials indicate that the Fe/Li is very effective in causing the small silt/clay particles to coagulate into larger particles that are easily filtered. On the basis of these data, the ex-situ dewatering of the Mound sediments should not be a problem if Fe/Li can be utilized.

IV.5.1.5 Effects of Washing

Figure IV.8 shows the effects of two successive washings of the filter cake on the dewatering time for various combinations of additives (all tests at 20 psig):

- Run #14: 10% Fe/Li,
- Run #17: 13% Fe/Li + 10% YWC,
- Run #18: 7% Fe/Li + 10% YWC,
- Run #25: 50% E-3098 + 25% YWC,
- Run #26: 50% 573C + 25% YWC, and
- Run #27: 17% Fe/Li + 25% YWC.

The dewatering time tended to increase for each washing because some of the flocculant or coagulant washed/rinsed out during the reslurrying and filtration process. The primary exception to this trend was Run #14, in which the dewatering time decreased during each washing. Because Run #14 was the only trial in which YWC was not added, it was deduced that the YWC tended to retain the moisture in the cake, leading to the longer filtration times.

IV.5.2 Filter-Press Simulation Tests

As indicated in the previous sections, effective sludge pretreatment can increase sludge filterability and washability by more than an order of magnitude. The sludge pretreatment additives found to be the most effective in the screening tests were Fe/Li and two cationic polymers made by American Cyanamid, 573C and E-3098.

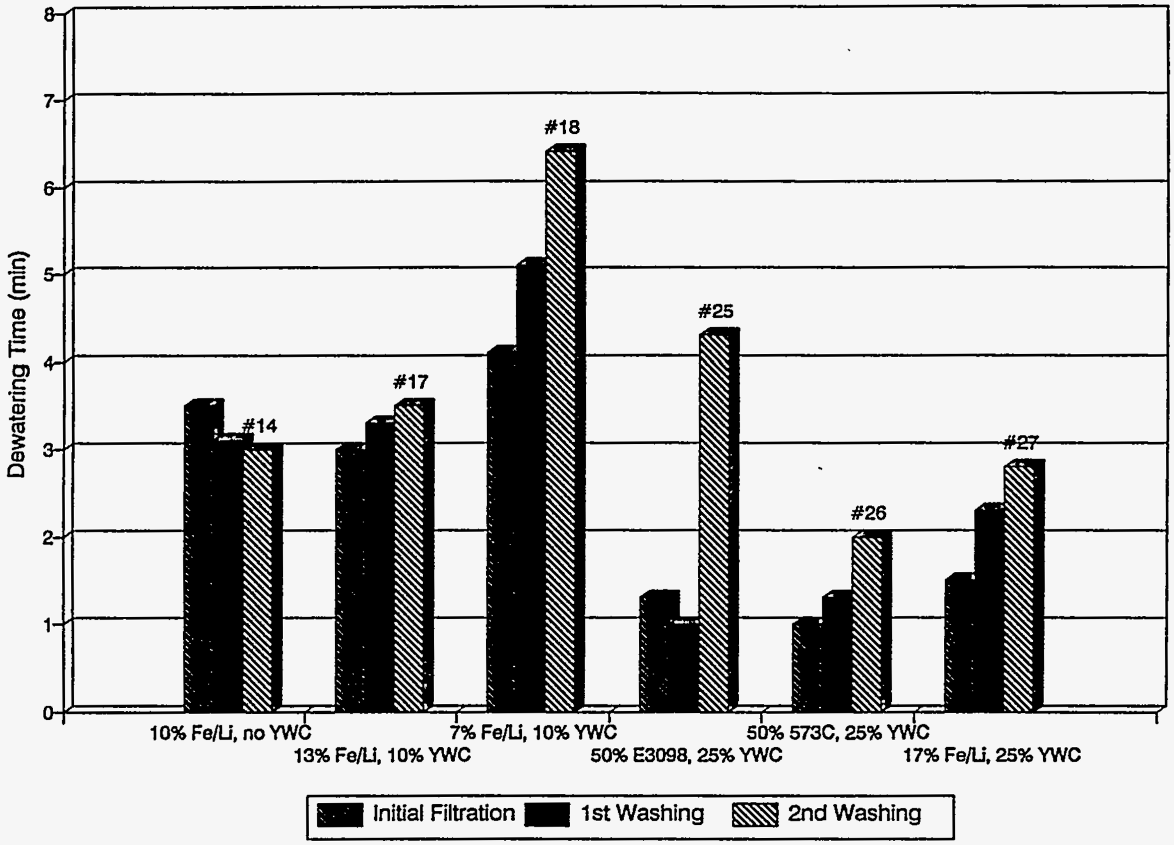


FIGURE IV.8 Effects of Washing of the Filter Cake on the Dewatering Time for Various Combinations of Additives

IV.5.2.1 Discussion of Simulation-Test Results

The effectiveness of the three most successful pretreatment options was quantified further by JWI filter-press simulation runs. The data from these tests were tabulated in Table IV.5. Pertinent observations about the tests and data include the following:

- Filter-cake formation was essentially complete in all three trials after about 15 min, although the E-3098 trial was allowed to run for 25 min. Trial completion was indicated by a relatively constant, low flow of filtrate. Figure IV.9 depicts the progress of the filtrations with respect to the cumulative flow (generation) of filtrate.

- The filter cake from the Fe/Li trial appeared to be the best, both qualitatively (appearance, feel) and quantitatively (density, percent solids).

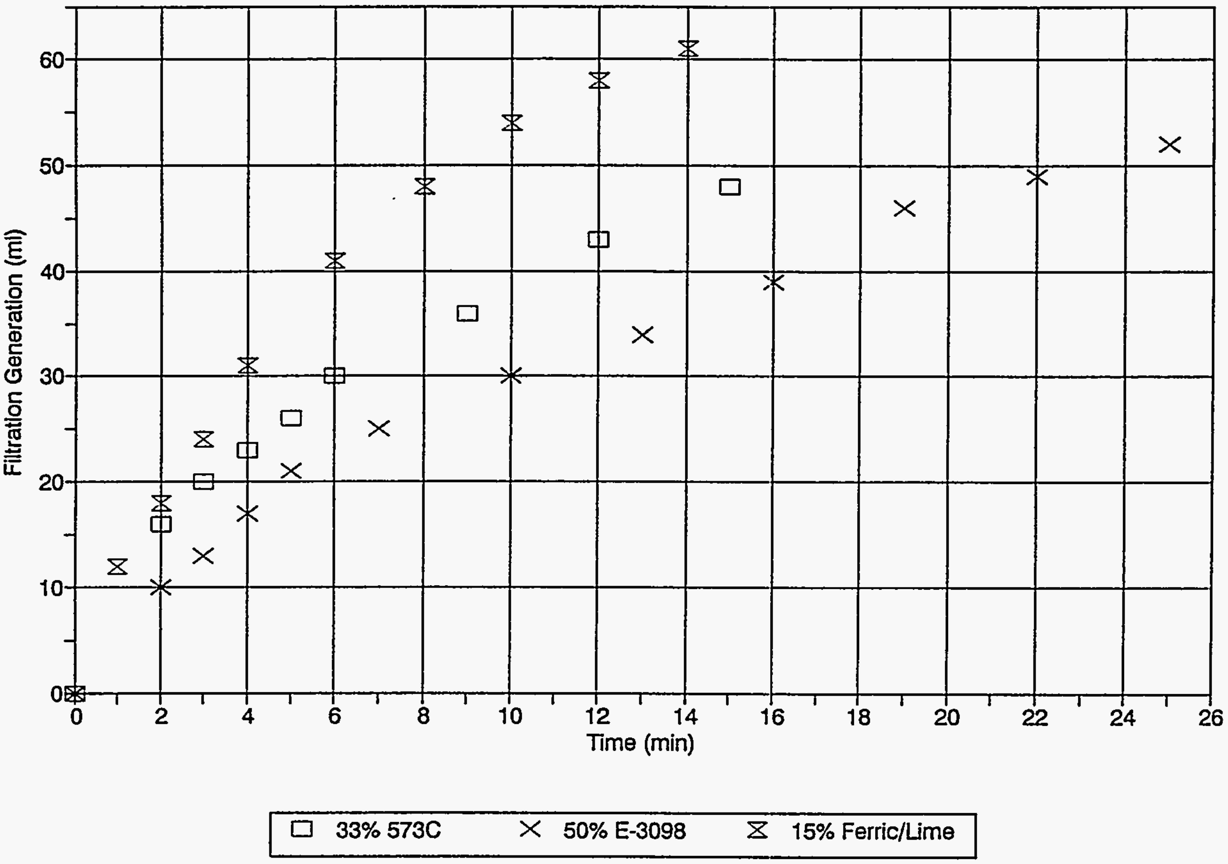


FIGURE IV.9 Filtrate Generation versus Time (JWI Lab-Press Tests)

- The Fe/Li treatment produced the largest quantity of filtrate (and highest-solids-content filter cake). The pH of the Fe/Li filtrate was slightly higher (9.3) than the pH in the filtrate from other two runs (8.6 to 8.8).

- The washing and air drying of the Fe/Li cake proceeded very quickly, with a flow rate of almost 18 mL/min for the three cake volumes of wash solution. The effectiveness of the washing could not be determined on the basis of these tests, because no quantitative measures were made for the target solutes.

IV.5.2.2 Scale-Up Analysis

The test results listed in Table IV.5 were scaled up, using RUST's computer programs, to predict full-scale, ex-situ dewatering/washing operations. Assuming a 92-ft^3 filter press would be used for the ex-situ dewatering/washing operation, the predicted performance data for these three sludge pretreatment options were normalized on the basis of original sediment solids. The results of this analysis are shown in Table IV.6.

TABLE IV.6 Comparison of Three Ex-Situ Dewatering Options (using a 92-ft^3 recessed plate filter press)

	Solids Processing Data		Filter-Cake Data		Filtrate/Rinsate Data		
Pretreatment Option	Cycle Time (min)	Ton Solids/ Batch	Cubic Ft/ Ton Solids	% Solids	Gallon/ Batch	Gallon/ Ton Solids	Quality (clarity)
Fe/Li	85	2.91	63.2	64.7	2,194	1,508	clear
573C	85	2.67	68.9	60.8	2,167	1,623	clear
E-3098	95	2.27	81.2	54.5	2,151	1,899	cloudy

As graphically indicated in Figure IV.10, both Fe/Li and 573C pretreatment resulted in a batch cycle time of 85 min, including 15 min of filter-cake washing with three cake volumes of water. Pretreatment with the E-3098 polymer resulted in a 95-minute batch cycle time. Figure IV.10 also shows that more original sediment solids can be processed in each filter-press batch when Fe/Li is used, even though this method results in addition of solids (ferric hydroxide and undissolved lime) to the sludge. This processing increase occurs because the filter cake produced with Fe/Li contains significantly more solids than filter cakes produced by using the other two pretreatment methods. The higher cake solids content from the Fe/Li pretreatment results in a smaller volume of filter cake. These two comparisons, filter-cake generation rate and solids content, are shown graphically in Figure IV.11.

The volumes of filtrate and rinsate generated from the ex-situ dewatering/washing operation for the three pretreatment options are shown in Figure IV.12. Again, the Fe/lLi pretreatment shows the most favorable results. The total volume of filtrate and rinsate generated with Fe/Li pretreatment is about 400 gal/ton of original solids. In comparison, approximately 425 and 495 gallons are generated per ton of original solids for the 573C and E-3098 pretreatment methods, respectively.

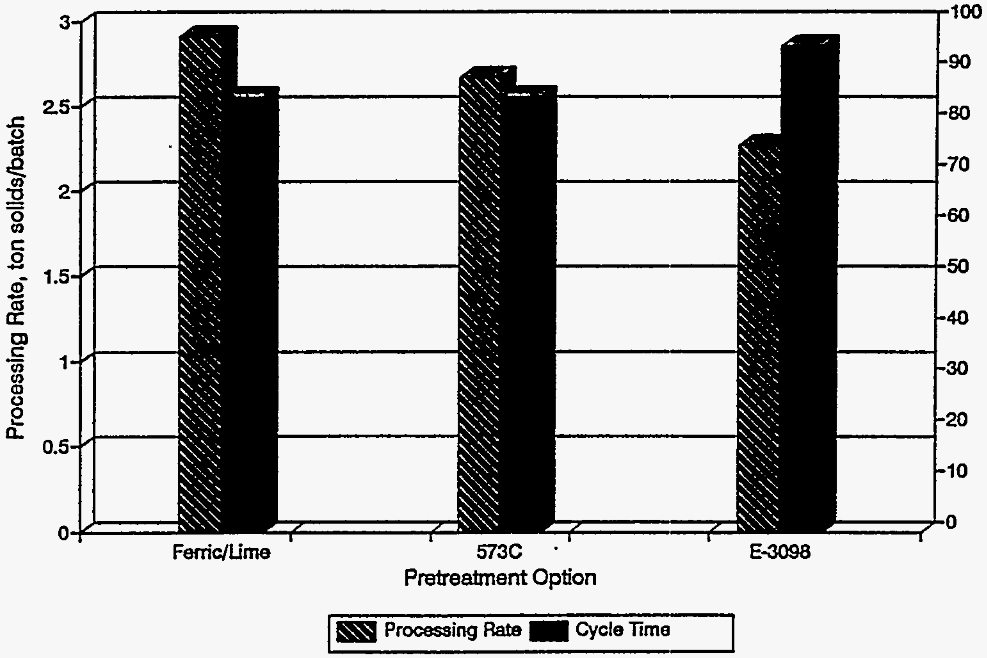


FIGURE IV.10 Solids Processing Comparison (dewatering scale-up analysis)

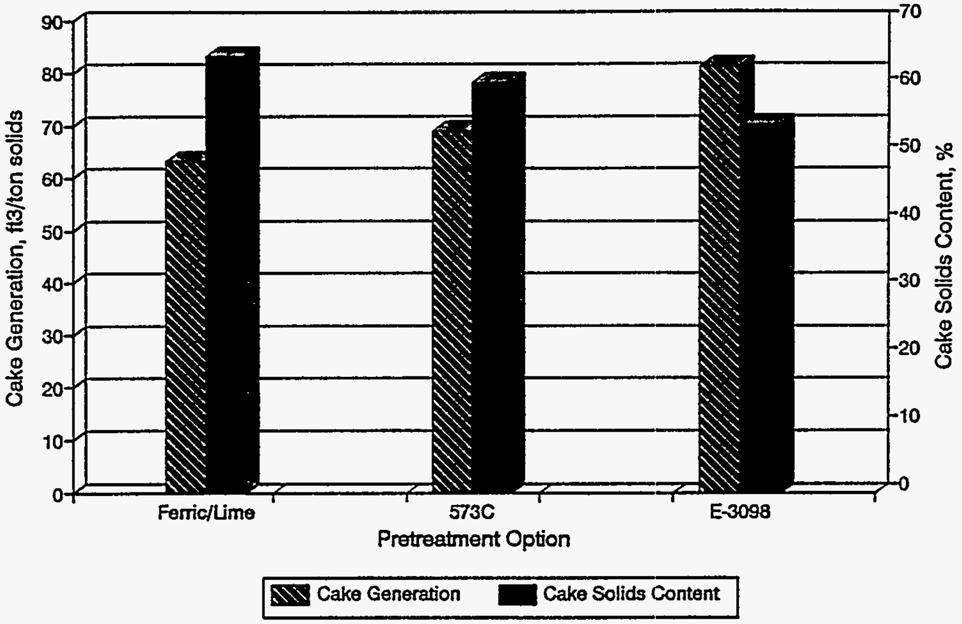


FIGURE IV.11 Filter Cake Comparison (dewatering scale-up analysis)

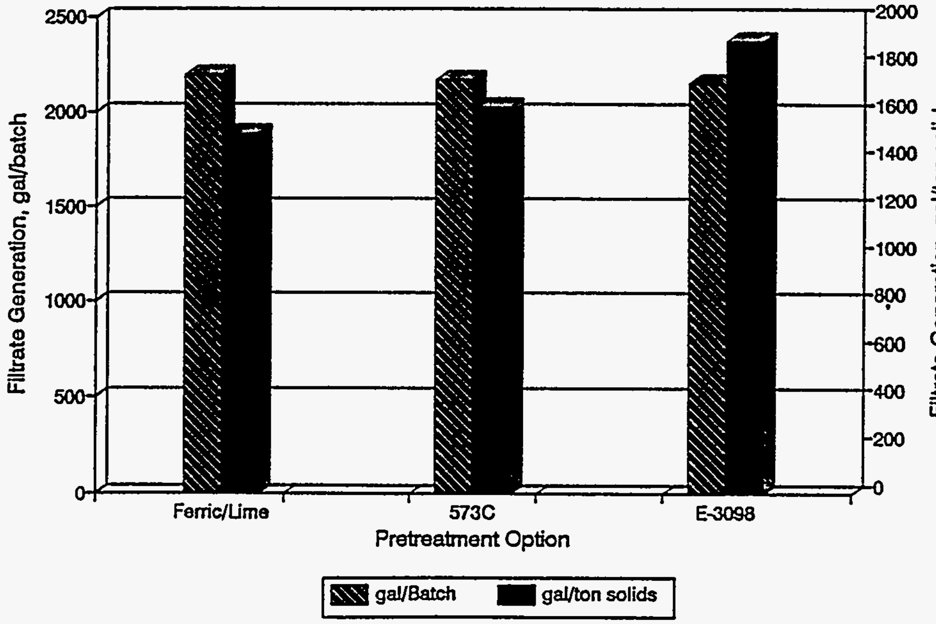


FIGURE IV.12 Filtrate/Rinsate Comparison (dewatering scale-up analysis)

IV.6 Summary and Recommendations

The ACT*DE*CON^{SM}-treated sediment from the Mound site presents a formidable problem with respect to the separation of the wash/rinse solutions (and entrained contaminants) from the solid particles. For an ex-situ treatment process, the problems do not appear to be insurmountable. However, a significant amount of further study is required to assess the feasibility of in-situ application of the treatment processes to the Mound sediments.

The following summary comments and recommendations are based on the results of the tests described in Section IV.4 and RUST's previous experience in dewatering a variety of sludges and soils.

- **Ex-Situ Dewatering Approach:** Based on the results from the filter press simulation tests, it appears that the ACT*DE*CON^{SM}-treated Mound sediments can be readily dewatered by using conventional pressure-filtration equipment. A scale-up analysis showed a reasonable press cycle time (85 minutes) and a high filter cake solids content (65%) when using a 92-ft^3 press and Fe/Li pretreatment.

- **In-Situ Dewatering Approach:** The testing results were inconclusive with respect to developing a process that would allow the Mound sediments to be treated and dewatered in-situ, where the primary driving force for the dewatering is gravity. However, the tests did show that the treated sediments can be drained under low pressure and vacuum conditions by adding Fe/Li and YWC. Further testing under simulated field conditions (gravity drainage and MecTool-type injection and mixing) is required to assess the feasibility of this approach.

- **Effects of Additives on Radionuclide Removal:** All of the testing was conducted on a surrogate ACT*DE*CON^{SM} soil slurry. The primary focus of the evaluation was to define the hydraulic parameters associated with removal of water from this fine soil particle matrix. The additives used to achieve effective dewatering of the slurry may have an adverse affect on the removal of radionuclides from the soil (e.g., causing them to be retained or redeposited). Measurement of this phenomenon was beyond the scope of this work and will have to be fully investigated in the next phase, to ensure that the ACT*DE*CON^{SM}-solubilized radionuclides are removed from the soil during the dewatering process.

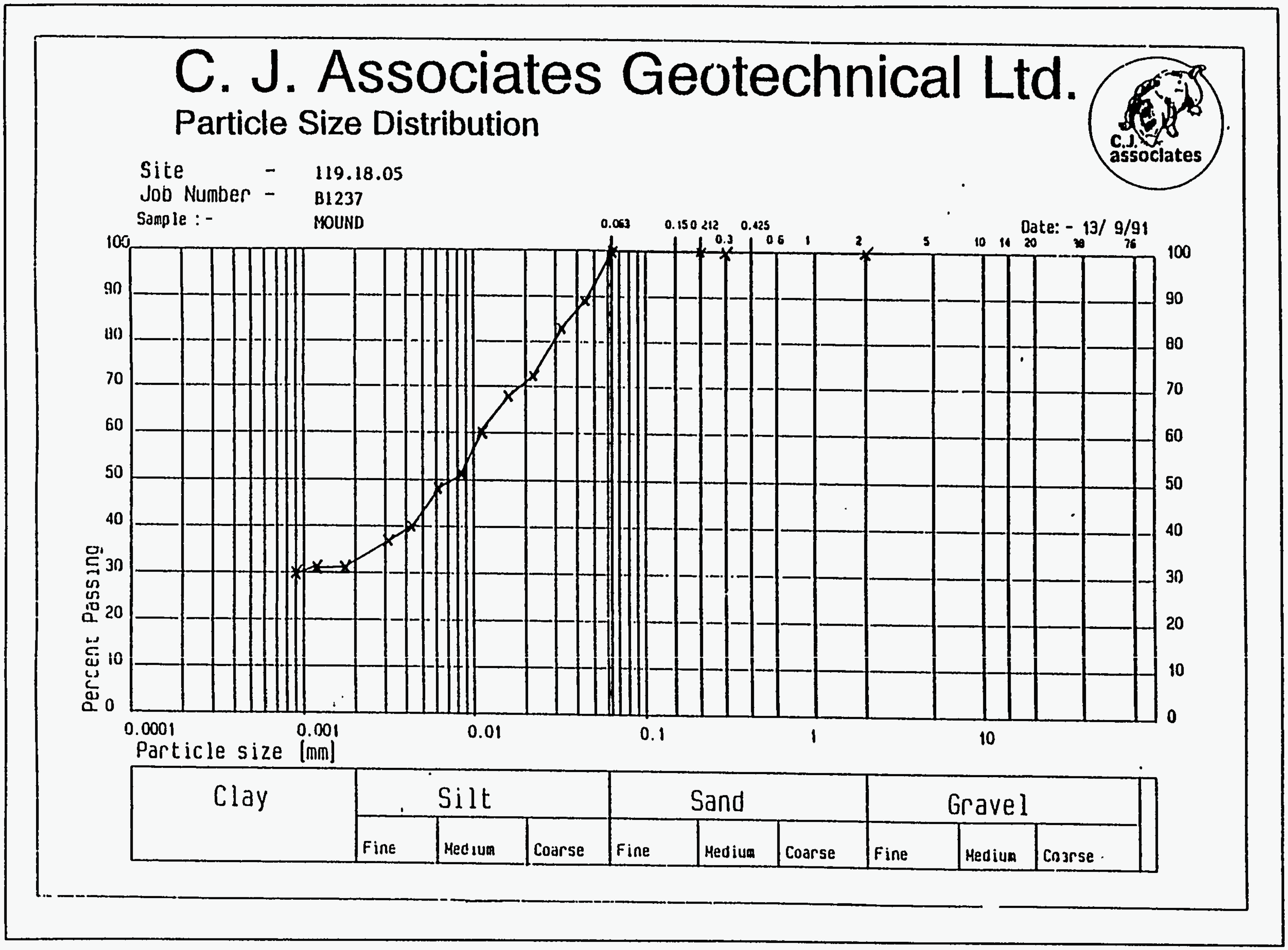
Appendix IV.A:

Mound Sediment Characteristics — Report Excerpts

SIZE RANGE, μM	% WEIGHT	% Pu-238
> 2000	-	-
2000 - 840	1.9	-
840 - 250	4.0	-
250 - 125	2.8	-
125 - 53	3.7	-
53 - 20	22.2	6.4
20 - 5	28.4	12.3
5 - 2	7.2	11.8
< 2	29.7	69.5

* **Tamura, T., "Physical and Chemical Characteristics of Plutonium in existing Contaminated Soils and Sediments",in Transuranium Nuclides in the Environment, IAEA, Vienna (1976), Paper number IAEA-SM-199/52, Pg 213**

Excerpted from Rogers, D.R., 1992, "Properties of Pu-238 Contaminated Clay Deposits in the Miami-Erie Canal," EG&G Mound Applied Technologies, Miamisburg, Ohio. Prints of slide-show compilation of data by D.R. Rogers and others.



C. J. Associates Geotechnical Ltd.

Particle Size Distribution

Site - 119.18.05
Job Number - B1237
Sample : - MOUND

Date: - 13/ 9/91

Excerpted from Brown, K.A., R.R. Heinrich, D.O. Johnson, and D.E. Edgar, 1992, "Preliminary Laboratory Study of Plutonium-238 Dissolution from Mound Soil by Means of the ACT*DE*CON^{SM} Process," Argonne National Laboratory report ANL/ESD-15, April.

	LAB REPORT: CHEMICAL ANALYSIS									
	MOUND, FERNALD SOIL SAMPLES									
	RECEIVED IN LAB ON: 7/93									
METHOD	TEXTURE/HYDROMETER-24 HR METHOD									
	MEDIUM, COARSE, AND VERY COARSE SAND	VERY FINE SAND	COARSE SILT	MEDIUM SILT	FINE SILT	VERY FINE SILT	COARSE CLAY	MEDIUM CLAY	FINE CLAY	TEXTURE CLASS
UNITS (micrometers)	>100	63 to 100	32 to 62	17 to 31	9 to 16	5 to 8	3 to 4	>1 AND <2	<1	
PERCENT	%	%	%	%	%	%	%	%	%	
SAMPLE										
FERNALD CLEAN SOIL	47.50	3.75	7.50	20.00	2.50	5.00		13.75		LOAM
FERNALD CLEAN SOIL DUPLICATE	46.25	3.75	10.00	17.50	2.50	2.50		17.50		LOAM
MOUND SOIL COMPOSITE Non Spiked, Non Treated	15.00		6.25	11.25	20.00	15.00		32.50		SILTY CLAY LOAM
MOUND-DUPLICATE Non Spiked, Non Treated	10.00		8.75	12.50	18.75	16.25		33.75		SILTY CLAY LOAM
Date Analyzed:	7/26/93									
Analyst:	TAYLOR									

Excerpted from Analytical Report — Chemical Analysis of Mound, Fernald Soil Samples (duplicate analyses at ANL). Date Analyzed: July 26, 1993. Analyst: Taylor.

Mound-ACT*DE*CON^{SM} Feasibility Study, Phase II: Final Report

Chapter V

Conclusions and Future Work

December 1994

Chapter V

Conclusions and Future Work

The objective of the Mound-ACT*DE*CON^{SM} Feasibility Study is to provide the U.S. Department of Energy (DOE), Office of Technology Development, and Mound with a workable alternative for the treatment of the plutonium-contaminated soil found at the Mound site and sediment found at the Miami-Erie Canal adjacent to the Mound site. Specifically, the purpose of this project is to demonstrate the ability of the ACT*DE*CON^{SM} process to reduce the plutonium contamination in the Mound site sediment to an acceptable level. The ACT*DE*CON^{SM} process involves a highly selective dissolution of the contaminant from the soil/sediment by means of a chemical wash.

In Phases I and II, the effectiveness of ACT*DE*CON^{SM} and MAG*SEP^{SM} were tested on a laboratory scale. Phase I (1992) demonstrated in a preliminary laboratory study the dissolution of ^{238}Pu from Mound soil by means of the ACT*DE*CON^{SM} process. Phase II (1993-1994) of the project provided critical information that was used to achieve a better definition of the process parameters. This critical information can be summarized as follows:

- Spiking of clean Mound soil does not mimic the plutonium forms that are present in the Mound soil/sediment. In other words, weathering has changed the way plutonium is held in/onto the soil/sediment from its original plutonium nitrate form.

- The ACT*DE*CON^{SM} formulation originally optimized for the spiked soil was not as effective in removing plutonium from weathered Mound soil/sediment. A stronger formulation was subsequently optimized to effectively remove plutonium from the weathered soil/sediment.

- The dissolution of nonhazardous minerals was contained at acceptable levels.

- The MAG*SEP^{SM} filter was able to remove the magnetic particles from spent ACT*DE*CON^{SM} solution containing up to 5% solids. However, the particle-coating ion-exchanger previously found to remove plutonium from spent ACT*DE*CON^{SM} solution did not prove effective in this process when the ACT*DE*CON^{SM} solution had been used in the decontamination of contaminated Mound material.

- The intrinsic composition of the Mound soil/sediment (very high clay content) represents a worst-case scenario for materials-handling/dewatering issues. Customizing the various treatments to fit this specific case is a more complex issue than it would be for other cases.

- Further action is needed to adjust the ACT*DE*CON^{SM} chemistry for optimizing the treatment of Mound soil.

- An in-situ approach is not in the best interest of DOE and Mound for a number of economic, technological, and environmental reasons. Future work should focus on ex-situ developments.

- Commercially available technologies should be investigated to develop the most cost-effective method for applying the ex-situ process in the field.

Phase II work was completed in September 1994, with the determination of the residual plutonium's mobility in the treated soil. At that time, however, no effective ion exchanger able to remove the plutonium from the spent ACT*DE*CON^{SM} had been identified. Therefore, the MAG*SEP^{SM} portion of the original project was set aside for further development after the final ACT*DE*CON^{SM} composition is optimized.

Future work will need to document the process conditions necessary for ACT*DE*CON^{SM} to remove plutonium from Mound sediment in order to achieve Mound site and regulatory goals. The program will determine the optimal physical and chemical conditions necessary to demonstrate the ability of an integrated pilot-scale treatment system to achieve the cleanup of the contaminated Mound sediment. A quantitative objective is to achieve a final plutonium activity level below 25 pCi/g in the sediment at its natural moisture status. Testing will be designed initially to optimize the application conditions, with the ultimate objective of achieving the goal of activity below 25 pCi/g.

Phase III will comprise multiple tasks associated with preparation for the pilot-scale test. During Phase III, an engineering and economic scaleup review will be performed to evaluate the scaleup to a pilot-scale demonstration by using the SOIL*EX™ System. Issues important to Mound and the regulators will be identified, and how those issues will be addressed during the pilot-scale demonstration will be determined. The work will include defining the hardware modifications and operational guidelines for conducting the pilot-scale simulation.

Work in Phase III will take into consideration the information obtained during Phase II and additional direction provided by DOE management. The work program will have the purpose of refining the technology sufficiently to allow a demonstration using the SOIL*EX™ pilot-scale equipment. The SOIL*EX™ pilot plant was designed, constructed, and operated to support the INEL Pit 9 interim action. The pilot plant is a fully integrated process system designed to demonstrate the ability of the ACT*DE*CON^{SM} chemistry to operate effectively at the pilot scale. In a proof-of-process demonstration conducted in late 1993, the SOIL*EX™ pilot plant successfully demonstrated the removal of spiked surrogate contaminants from actual INEL Pit 9 soil/sludges. Due to the high organic and clay content in the Mound sediment, a purely in-situ approach to the application of the ACT*DE*CON^{SM} process is not feasible. The ex-situ application using the SOIL*EX™ system is considered to be a more pragmatic approach.

Studies performed during qualification of the process for INEL Pit 9 have demonstrated that Denver Cell results can be correlated with the SOIL*EX™ pilot plant performance. Thus, a series of Denver Cell tests will be conducted in Phase III on contaminated Mound soil/sediment to determine the feasibility of conducting a successful pilot-scale test on the Mound site sediment.

The first task under Phase III will constitute a proof-of-process evaluation of the proposed process formulations. The purpose is to demonstrate, by using Denver Cells, the effectiveness of ACT*DE*CON^{SM} in removing plutonium from Mound sediment. The formulation evaluated in the Denver Cell bench-scale tests will be the one developed during laboratory-scale testing in Phase II that reduced the plutonium concentration in Mound site sediment to an acceptable level.

The second task will use the most successful chemistry to evaluate the process kinetics. A range of acceptability for each of the process parameters (or combinations thereof) will be defined. The value of the parameter number (between these limits) needed to achieve an acceptable decontamination will be evaluated. A series of laboratory-scale batch treatment tests in Denver Cells will determine the effects of variations of certain process parameters on the removal of plutonium from the Mound sediment, as measured by the plutonium activity. The primary objective is to determine the conditions that provide the lowest possible final activity, while also generating the smallest quantity of residuals that require secondary treatment and/or disposal.

A task to further investigate the application and characteristics of the sediment/solution mixing system, and to define the best technology and combination of filter aids for ex-situ dewatering of the sediment, will be included in the Phase III work. The contaminated Mound sediment is composed predominantly of fine silt and clay particles, which typically exhibit very low permeability and tend to retain water (and dissolved contaminants), especially when exposed to sodium ions. Filter aids are usually required to enhance the dewatering/drainage of these types of materials. The use of various types of filter aids, both physical additives and flocculating/coagulating agents, has been investigated as part of the expanded Task 13 from Phase II. The objective of the Phase II work was to select the types of additives required to effectively dewater and wash the ACT*DE*CON^{SM}-treated sediment. The results indicated that certain additives could decrease the time required to dewater the sediment slurry by more than an order of magnitude. Even though the tests were conducted with batch laboratory-scale dewatering test equipment, it was assumed that the selected filter aids would also be able to enhance the dewatering/drainage of the ACT*DE*CON^{SM}-treated sediment in an ex-situ process application. A series of bench-scale simulation tests on clean sediment will compare various dewatering additives for the treated Mound soil and canal sediment. The primary objective of this work will be to determine the types and quantities of filter aids that provide the most effective dewatering. The effects of the additives on the plutonium chemistry will also be evaluated.

The Phase IV work will demonstrate that the Mound sediment can be decontaminated on a continuous solids feed basis by using the SOIL*EX™ pilot-plant-scale equipment. The SOIL*EX™ system, active and currently located at the Clemson Technical Center, has been successfully used as part of the Pit 9 demonstration project.

After successful demonstration of pilot-scale testing, Phase V of the program will be a field demonstration and remediation of the canal sediment.