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TREATMENT OF PLUTONIUM CONTAMINATED SOIL/SEDIMENT FROM THE MOUND SITE USING THE ACT*DE*CON[SM] PROCESS

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ABSTRACT

The removal and/or treatment of contaminated soil is a major problem facing the U.S. Department of Energy (DOE). The EG&G Mound Applied Technologies site in Miamisburg, Ohio, has an estimated 1.5 million cubic feet of soil from past disposal and waste burial practices awaiting remediation from plutonium contamination. This amount includes sediment from the Miami-Erie Canal that was contaminated in 1969 following a pipe-rupture accident. This sediment has a high silt and clay content. Approximately 80% of the sediment particles are less than 32 μm, with 33% less than 2 μm. As expected, most of the plutonium is associated with the smaller soil particles. Conventional soil washing techniques that use particle separation would generate too large a waste volume to be economically feasible. Therefore, innovative technologies are needed for the cleanup.

A joint project by Argonne National Laboratory (ANL), SELENTEC, and Rust Clemson Technical Center is currently under way to investigate the ACT*DE*CON[SM] process. This project is funded by the Office of Science and Technology, within DOE's Office of Environmental Management, under the Subsurface Contaminants Focus Area.

The ACT*DE*CON[SM] process was developed by SELENTEC for washing soils to selectively dissolve and remove heavy metals and radionuclides. ACT*DE*CON[SM] chemically dissolves and removes heavy metals and radionuclides from soils and sediments into an aqueous medium. The ACT*DE*CON[SM] process uses oxidative carbonate/chelant chemistry to dissolve the contaminant from the sediment and hold the contaminant in solution.

Earlier phases of this project involved the laboratory-scale optimization of the ACT*DE*CON[SM] solvent formulation, as well as the demonstration by soil analysis that the contaminants can be removed without dissolving any significant amount of the nonhazardous minerals. Application conditions were developed from the lab-scale testing that reduced the plutonium level in the Mound soil/sediment to an acceptable level.

Mobility studies, as dissolution coefficient (K_d) studies, were also conducted on the ACT*DE*CON[SM]-treated soil/sediment in order to evaluate the effect of the treatment on the potential release of the residual plutonium in mobile forms into the environment (groundwater, plants).

The objective of recent work was to document the process conditions necessary to achieve the Mound-site and regulatory-cleanup goal. The cleanup goal was set at 75 pCi/g (for soil at its natural moisture status), while a level of 25 pCi/g was established for soil excavation. The test program was designed to optimize the application conditions based on a starting activity in the contaminated soil of 300 to 600 pCi/g. Various application conditions were investigated under proven scale-up conditions to engineer the pilot-scale application. Percent removal of plutonium has exceeded 96%, which translates into a decontamination factor of >16. Higher removals were achieved through optimization of solids loading, kinetics, rinse solution composition, temperature control, and multiple extraction stages.

Since the contaminated Mound soil consists predominantly of fine silt and clay particles, which typically exhibit very low permeabilities and tend to retain water, especially when exposed to handling, effective means for the separation of solids from liquids were investigated, as well as the possible interactions

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between filter aids and the plutonium dissolution chemistry.

Future work will aim at demonstrating at an integrated pilot-scale level the physical and chemical conditions at which the ACT*DE*CON^{SM} process is able to clean up the Mound sediments. In a proof of process demonstration conducted in late 1993, a pilot-scale ACT*DE*CON^{SM} extraction system was used to successfully demonstrate the removal of spiked surrogate contaminants from actual INEL Pit 9 soil/sludges. The same approach is being adapted to the Mound conditions. Pilot-scale testing is expected to be carried out in late 1996.

I. INTRODUCTION

The removal and/or treatment of contaminated soils is a major problem facing the U.S. Department of Energy (DOE) and the U.S. Environmental Protection Agency (EPA). The EG&G Mound Applied Technologies site in Miamisburg, Ohio, has an estimated 1.5 million cubic feet of soil from past disposal and waste burial practices for possible remediation.

A portion of the abandoned Miami-Erie Canal paralleling the Greater Miami River receives the runoff and the storm water discharge from the Mound Laboratory. In 1969, a low-level plutonium leak contaminated soil and sediment as far away as 1.5 miles downstream of the old canal system. An estimated 700,000 cubic feet of soil/sediment requires remediation.

The canal is adjacent to a city park and overlies the Buried Valley Aquifer, which is 20 feet below. An estimated 5 Ci of plutonium 238 (half-life 87.4 years) is in the canal sediment.

The sediment from the canal has a high silt and clay content. Approximately 80% of the sediment particles are less than 32 μm, with 33% less than 2 μm. As expected, most of the plutonium is associated with the smaller soil particles. Conventional soil washing techniques that use particle separation would generate too large a waste volume to be economically feasible. Therefore, innovative technologies are needed for the cleanup.

A joint project by Argonne National Laboratory, SELENTEC, and Rust Clemson Technical Center is currently under way to investigate the ACT*DE*CON^{SM} process. This project is funded by the Office of Science and Technology, within DOE's Office of Environmental Management, under the Subsurface Contaminants Focus Area.

II. PROCESS DESCRIPTION

SELENTEC has developed the ACT*DE*CON^{SM} process for use in soil and sediment washing to chemically dissolve and remove metal and radioactive contaminants. The process uses oxidative carbonate chemistry to dissolve the contaminant from the sediment and a chelating agent to complex and hold the contaminant in solution. The process combines dissolution with dilute selective solutions, contaminant recovery, and solution regeneration to provide a continuous recirculating process for the treatment of soils and sediments to remove strontium, cesium, technetium, radium, actinides (uranium and transuranics), barium, lead, and mercury. A variety of chemical concentration ratios can be utilized.

The actinide solution chemistry combines established carbonate recovery chemistry with a chelant in an oxidative environment. The oxidant is required to raise the oxidation state of the contaminant. For example, when plutonium is present in an oxidation state lower than IV, an 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 is observed to be an important factor in the formation of soluble complexes.

III. BACKGROUND

The goal of this project is to optimize the ACT*DE*CON^{SM} process for use at the Miami-Erie Canal site and to evaluate the effects of treatment on such soil/sediment characteristics as revegetation potential (revegetation is critical since it controls erosion and dust emission) and on mobility of the residual plutonium in the treated material.

Earlier phases of the program involved the lab-scale optimization of the ACT*DE*CON^{SM} solvent formulation, as well as demonstration, by sediment analysis, that the contaminants can be removed with minimal dissolution of the nonhazardous minerals present in the sediment. Various formulations of ACT*DE*CON^{SM} were evaluated during these phases to identify the optimum contaminant removal conditions.

Initially, testing was performed on simulated contaminated sediment. Clean sediment was spiked with plutonium in a manner that simulated how the sediment originally became contaminated. An optimized ACT*DE*CON^{SM} formulation was developed that reduced the plutonium levels in the simulated sediment. Retesting this formulation on actual canal sediment demonstrated that the plutonium had changed over the years due to environmental factors and that the extractants which worked on spiked sediment were

ineffective in removing plutonium from the actual, contaminated samples.

The sediment was then examined in a speciation study to evaluate how the plutonium was bound with the sediment. This study involved a series of solvent extractions and total acid dissolution of the final sediment. The fraction of plutonium removed by each extraction was related to a specific association of the plutonium. Table 1 shows the fraction removed and the associated form for the plutonium in untreated sediment, sediment treated with an ACT*DE*CON^{SM} formulation optimized for spiked soils, and sediment treated with the modified ACT*DE*CON^{SM} formulation shown to be effective for the contaminated canal sediment.

The analysis of the sediment shows that the majority of the plutonium is either complexed with the organic material in the sediment or is associated with oxides. A small fraction of the plutonium is classified as residual. The residual plutonium was analyzed by total dissolution of the sediment and is considered to be in a form that is either fused with the sediment or chemically complexed with the sediment particles. A very small fraction of the plutonium is readily removed from the sediment by water or by a salt extraction. The speciation study proved that, in order for the ACT*DE*CON^{SM} to work, its effectiveness on plutonium bound to soil oxides, needed to be enhanced.

Speciation analysis of the sediment treated with the modified ACT*DE*CON^{SM} formulation showed that significant reduction in the contaminant level could be achieved.

IV. MOBILITY STUDIES

Mobility studies were also conducted on the ACT*DE*CON^{SM}-treated soil/sediment in order to evaluate the effect of the treatment on the potential release of the residual plutonium in mobile forms from the treated soil to the environment (groundwater, plants). In these experiments six batches of contaminated sediment were treated simultaneously by the ACT*DE*CON^{SM} process. Some batches were then amended with a standard fertilized treatment of compost and nutrients and brought to a pH of 8.5 to improve condition for microbial life. The treated, treated and fertilized, and untreated sediment were then incubated at 18°C for 90 days. At four different times during the incubation period, a small aliquot of sediment was retrieved from each of the batches and contacted with Mound rainwater for six days. Total dissolution (fCi/L) and distribution coefficients (K_d) data were measured as functions of time and soil conditions after treatment (Figures 1 and 2).

These data indicated that a larger amount of plutonium was leached from the nontreated soil, probably as a consequence of the higher content of available/exchangeable plutonium, as compared to the treated soil. No increase in total relative mobility of the soil plutonium could be attributed, as a conclusion of these tests, to the treatment with ACT*DE*CON^{SM} under the testing conditions. In fact, ACT*DE*CON^{SM} treatment appeared to leave only the most insoluble forms of plutonium in the soil.

V. PARAMETRICS OPTIMIZATION

The primary objective of the parametric optimization work was to document the process conditions necessary to achieve Mound Site and regulatory cleanup goals of the canal sediment at its natural moisture state. The test program was designed to optimize the application conditions on the basis of a starting activity in the contaminated sediment of 300 to 600 pCi/g. Various application conditions were investigated with large bench-scale test equipment under proven scale-up conditions to develop an operating envelope for pilot-scale application and eventual full-scale application. In this phase of the project, the scale-up engineering and application costs were also evaluated, including the minimization of process inputs (reagents, power, etc.) and the maximization of treated soil as a fraction of the starting soil.

At the start of the test program, weather conditions limited access to the canal to obtain sediment for testing. The only materials available were two 5-gallon buckets containing 29 and 30 kilograms of sediment, which had been removed previously as a "hot spot" from the canal and were in storage at the Mound site. Approximately half of the material from each bucket was placed in a large Hobart planetary mixer and blended to homogenize. Analysis of duplicate grab samples provided an initial characterization of the sediment. The average plutonium-238 concentration was 2,545 pCi/g. Analysis of the metals content showed the sediment to be 7.2% calcium, 1.4% iron, 0.2% potassium, 2.4% magnesium, and 0.03% manganese. The bulk density was 1.2 grams per cubic centimeter and the percent moisture was 21.3. The activity in this sediment was considered to be much higher than the nominal average contaminant level of 400-600 pCi/g plutonium-238.

In the initial test work, several of the individual application parameters for ACT*DE*CON^{SM} were examined. This work included a head-to-head comparison of several of the chelants available for the formulation. The tests were carried out using a D-12 mixer having an attrition scrubber blade (two opposing pitched propeller blades). The test scenario had been demonstrated in other programs to provide results under scale conditions.

Previous laboratory testing had used ethylenediaminetetraacetic acid (EDTA) as the chelant. In the current extraction tests, diethylenetriamine-pentaacetic acid (DTPA) and citric acid were compared with EDTA. DTPA provided slightly better results than EDTA, which was significantly better than citric acid. In a single wash application >85% of the activity was removed. Since the advantages of using DTPA were slight, EDTA was used for subsequent testing, because of the higher level of experience, the unknown environmental impact of DTPA, and the economic costs of using EDTA.

Additional parameters that were investigated by the testing protocol included application time, temperature, solids loading, chemical concentration and types of rinsing solutions. In investigating each parameter, testing conditions were used that were similar to those used in or derived from previous tests. The conditions that were chosen as best-performing were a two-stage extraction with a rinse at 70°C; a 10% solids loading with a 2-hour contact per stage; a 15-minute rinse contact; and the previously optimized extraction chemistry and pH.

Elevated temperature slightly increased the rate of plutonium removed but also increased the dissolution of the sediment. Higher solids loadings of up to 15% were tested and showed 10% solids plutonium removal but at a lower rate.

The kinetics of the process were investigated to evaluate the effect of extended solution contact. Sampling of the wash solution on an hourly basis, for two hours over the first solution contact and four hours over the second, showed that there was very little plutonium uptake after the first hour of each contact.

A sequential (sequenced) extraction test was undertaken to evaluate the plutonium levels achievable from a full application. Sequential extraction closely models the effects of a countercurrent extractor (CCE), which is the expected method of application on a full scale. The results of the sequenced extraction showed that greater than 97% of the plutonium was removed from the sediment, achieving a level (corrected for natural moisture content) of 65 pCi/g. An additional wash solution and rinse contact reduced the plutonium level to less than 38 pCi/g.

Finally, a series of sequenced extraction runs were performed on a sample of canal sediment that had a plutonium contamination level considered to be closer to the typical activity of 400 to 600 pCi/g. This canal sediment, with an initial activity level of 810 pCi/g, was remediated to a level of less than 55 pCi/g for the sediment (corrected to natural moisture content).

VI. SOLID-LIQUID SEPARATION

Since the contaminated Miami-Erie Canal sediment consists predominantly of fine silt and clay particles, which typically exhibit very low permeability and tend to retain water, effective means for the separation of the solids from the liquids were investigated. The use of various filter aids in conjunction with commercially available filtering equipment was investigated, as well as the possible interactions between filter aids and plutonium dissolution chemistry.

Preliminary data showed that certain additives (both physical additives and chemical flocculating/coagulating agents) could decrease the time required to dewater the soil/sediment slurry by more than an order of magnitude, without significantly interfering with the plutonium removal rate. These preliminary tests were conducted by using batch, laboratory-scale, dewatering equipment. Samples of treated sediment were sent to various vendors of commercial dewatering systems to test which system would perform best. Results indicate that selected filter aids and systems should be able to significantly enhance the dewatering/drainage of the ACT*DE*CON^{SM}-treated soil in a full-scale application.

VII. ENGINEERING ASPECTS

Current work is aimed at demonstrating, at an integrated pilot scale, the physical and chemical conditions at which the ACT*DE*CON^{SM} process is able to clean up the Miami-Erie Canal sediments. In a proof of process demonstration conducted in late 1993, a pilot-scale ACT*DE*CON^{SM} extraction system was used to successfully demonstrate the removal of spiked surrogate contaminants from actual INEL Pit 9 soil/sludges. The same approach is being adapted to the Mound conditions. Pilot-scale testing is expected to be carried out in the summer of 1996, and after successful demonstration, full-scale application will begin.

The principal component of the equipment will be the CCE, consisting of an elongated tubular trough, inclined on one end. Inside the trough is rotor designed to create a pulsing action on the materials being handled. The rotor is slotted to allow for liquid flow.

Solid feed will enter the lower end of the unit and be propelled upward by the action of the rotor. The wash solution will be injected at the higher end of the unit and pass by gravity flow through the solid material in a countercurrent flow. A CCE theoretically has fourteen extraction stages in one shell, giving high extraction efficiency. The CCE will have various injection points to apply the ACT*DE*CON^{SM} solution, as well as wash water to rinse the cleaned sediment.

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Table 1. Plutonium Speciation in Miami-Erie Canal Sediment Before and After the Treatment with Two ACT*DE*CON^{SM} Formulations

Sediment Fraction	^{238}Pu Activity (pCi/g) Untreated Sediment	Optimum Formulation Treated Sediment	Modified Formulation Treated Sediment
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

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

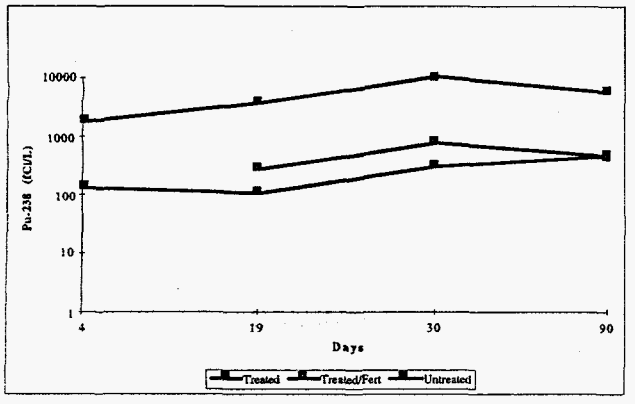
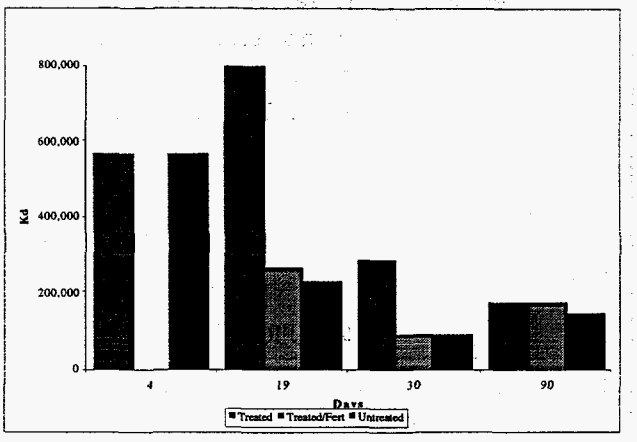


Figure 2. Plutonium Kd Values in the Four Contacts, Mean Values



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